Pall Corporation Comments To:

United States Environmental Protection Agency
Docket ID EPA–HQ–OAR–2011–0344
National Emission Standards for Hazardous Air Pollutants: Secondary Lead Smelting

Federal Register Volume 76, Number 97, pages 29032 to 29081, Thursday May 19th, 2011

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Pall Corporation is a Fortune 1000 Business and the world leader in filtration products. Pall has recently acquired an exclusive license to sell and manufacture the Xact* (previously manufactured by Cooper Environmental Services, LLC) an X-ray based continuous emissions monitor for lead and other metals.

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*Xact is a trademark of Cooper Environmental Services, LLC

1.0 Introduction

On May 19th, 2011 the EPA proposed new National Emission Standards for secondary lead smelters. As part of this proposal, EPA is expressly seeking comments and information on the use of lead (Pb) continuous emissions monitoring systems (CEMS) to monitor lead from point sources at these smelters saying:

> "We are seeing comments and information on the feasibility of applying this technology for monitoring lead emissions from these sources and the potential to require CEMS on existing sources in the source category."[1]

Pall Corporation (Pall) has recently acquired the exclusive license to sell and manufacture the Xact, an X-ray fluorescence based multi-metals continuous emissions monitor capable of monitoring up to 20 metals, including lead. This instrument has been used for several years as part of a hazardous waste incinerator's Alternative Monitoring Petition (AMP)[2] at Eli Lilly's Tippecanoe Laboratories. It has been Method 301 approved by the US EPA,[3,4] has been the recipient of the EPA's Clean Air Excellence Award,[5] and has passed annual relative accuracy test audits (RATAs) at Eli Lilly's hazardous waste incinerator for five years. This technology has demonstrated that it is reliable, produces accurate and precise concentration data, and can be used in a wide variety of applications on a diverse set of source types.

Pall believes that it is feasible to use this technology to measure source emissions from secondary lead smelters. In these comments, Pall is supplying data to show that the Xact has demonstrated:

1. Stable, reliable operation,
2. Accuracy,
3. Operation in a wide variety of sampling conditions, and
4. Wide measurement range that is more than adequate to meet the monitoring requirements of secondary lead smelters.

In addition to this data, Pall is proposing performance specifications and on-going quality assurance (QA) procedures for Pb CEMS that will 1) provide adequate demonstration of instrument accuracy, and 2) are general enough to be useful for many different types of potential lead measurement technologies. These performance specifications and on going QA procedures are those that have been used for several years to demonstrate the accuracy of the Xact as multi-metal CEMS and have been rewritten to specifically address lead. The performance specifications and on-going QA procedures can be found in Appendices A and B, respectively, of this document. In addition, we have provided supporting documentation on a reference aerosol generator that is used in the performance specification and as an annual auditing device for on-going QA. This document, *Traceability Protocol for Reference Aerosol Generators,*[6] was produced by Cooper Environmental Services, LLC as part of an EPA funded project.

2.0 Principle of Measurement

The Xact operates by withdrawing a large sample of stack effluent from the source and transporting it to a stilling chamber where the flow is slowed or stilled. A subsample of this main flow is then drawn through a reactive filter tape mounted on a reel-to-reel type tape drive. The filter tape captures both vapor phase and particulate phase metals. Following sampling, the sample deposit is automatically advanced into the analysis area where the deposited metal mass (including lead) is determined using X-ray fluorescence (XRF) while the next sample is collected. The stack concentration ($\mu g/m^3$) is determined by dividing the XRF determined mass (μg) by the total sample flow through the tape (m^3).

The core technologies of the Xact have been used extensively for years in a variety of applications. Reel-to-reel tape drives have been used for decades on beta gauge instruments that measure particulate matter (PM) in the air. There are literally thousands of operating instruments deployed utilizing this technology. XRF has been used in a wide variety of applications for years and has demonstrated that it is a rugged and robust technology. XRF has been used for metals measurement on Mars and the sea floor, and is now commonly used in handheld devices for determining Pb content in paint and for determining alloy types in scrap metal. The EPA has long approved the use of XRF for the measurement of metals on filter samples to determine the concentration of metals in ambient air. The procedures for making these measurements can be found in the EPA Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air[7] and are the basis for the XRF measurement methods used by the Xact.

3.0 Method 301 Approval

In 2005, the Xact demonstrated its measurement accuracy and precision on a thermal hazardous waste incinerator using EPA Method 301[8] which is the procedure by which new emissions measurement technologies are approved. During this test the Xact was challenged with aerosol concentrations traceable to NIST standards and containing arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg) and lead (Pb) at three different concentration levels (20, 60 and 130 $\mu g/m^3$). These concentrations were generated using a reference aerosol generator that was itself Method 301 approved. The average relative accuracy for all five metals over all three concentrations was 8.3%.[4] In addition, the linearity of the Xact's response over this measurement range was also determined by plotting the Xact reported concentration against the known aerosol concentration. A linear, least squares fit was performed and the results of this fit can be seen in Figure 1.[4]

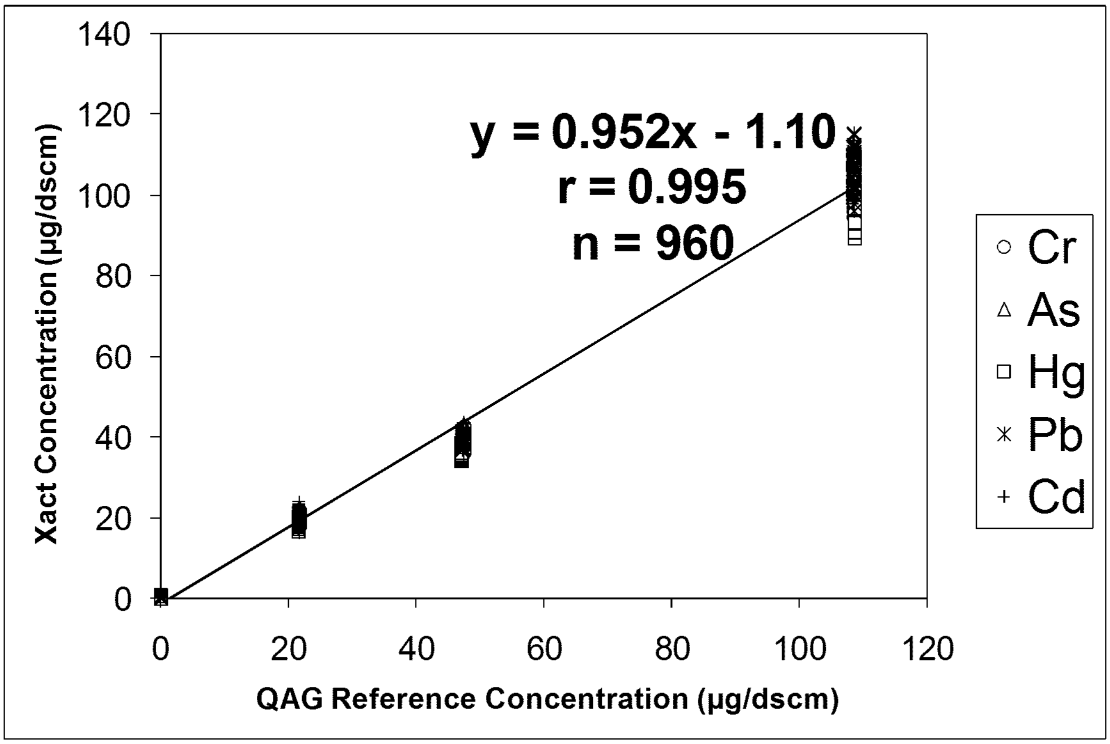

Figure 1. Xact Method 301 Results

The Xact passed all criteria required by Method 301 and was approved by the EPA for compliance monitoring on Eli Lilly's hazardous waste incinerator.

4.0 QA Procedures

The Xact determines concentrations in stack effluent by dividing the XRF determined metal mass by the volume of sample through the tape. The Xact utilizes several automated QA procedures to check the on-going accuracy of these two measurements. These QA procedures are outlined below and several of these QA procedures have been accepted by the EPA and published in the form of class C Other Methods.[9,10]

4.1. X-ray Fluorescence Quality Assurance

4.1.1. Stability check with every sample

X-ray fluorescence has the unique ability to be able to measure multiple elements simultaneously. This makes it possible to use a rare element, not likely to be present in the sampled aerosol, to check the stability of the Xact's XRF analyzer. The Xact does this by measuring the instrument's response to a palladium (Pd) rod fixed into a stable position under the sample tape. The Xact's response at the time of calibration is compared to the response during each and every sample analysis. This means that XRF analysis on every value reported by the Xact is quality assured.

4.1.2. Daily Upscale

One time each day, a rod with a small mass of metals on the tip is inserted into the analysis area. These metals are typically those most critical to measure, such as lead for a lead monitor. This technique checks the stability of the upscale response once per day.

4.1.3. Daily Zero or Blank

Additionally, the Xact analyzes a blank (unsampled) section of tape one time per day. This blank does not contain metals and this check helps insure that there is no contamination impacting the analysis for any of the key metals of interest.

4.1.4. XRF Audits

The Xact can also be audited periodically using thin film standards with certified areal concentrations in terms of $\mu g/cm^2$. These thin film standards consist of metals vapor deposited on Nucleopore[a] substrates. The mass of the standard is measured before and after the vapor deposit using a NIST traceable balance. These standards are produced commercially by Micromatter[b] and are recommended by EPA IO 3.3[7] for calibration of XRF equipment used to measure ambient filter concentrations. These standards can be inserted into the analysis area to check the accuracy of the XRF analyzer portion of the Xact™.

4.2. Flow Quality Assurance

4.2.1. Daily flow check

One time per day the flow measured by the Xact's sample flow meter is compared to the flow as measured by a second flow meter. This second flow meter is only used during this flow check and is calibrated to the same reference flow meter as the Xact's sample flow meter. This check ensures the stability of the Xact's sample flow meter.

4.2.2. Flow Audits

The sample and quality assurance flow meter can be checked periodically using a NIST traceable reference flow meter to ensure the accuracy of the flow measurements.

4.3. Total Instrument Checks

On an annual basis, the Xact can be challenged with a reference aerosol with concentrations traceable to NIST standards. This procedure involves dynamically spiking the Xact at a point as close as possible to the probe and comparing the spiked concentration to the concentration reported by the Xact over a range of concentrations. This procedure challenges the entire Xact system including the transport line, the

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[a] Nuclepore is a registered trademark of Whatman, Inc.
[b] Micromatter is a registered trademark of Advanced Applied Physics Solutions

sampling system, and the XRF analyzer. Figure 2 shows a diagram of the dynamic spiking arrangement as it has been performed as part of an Alternative Monitoring Petition.

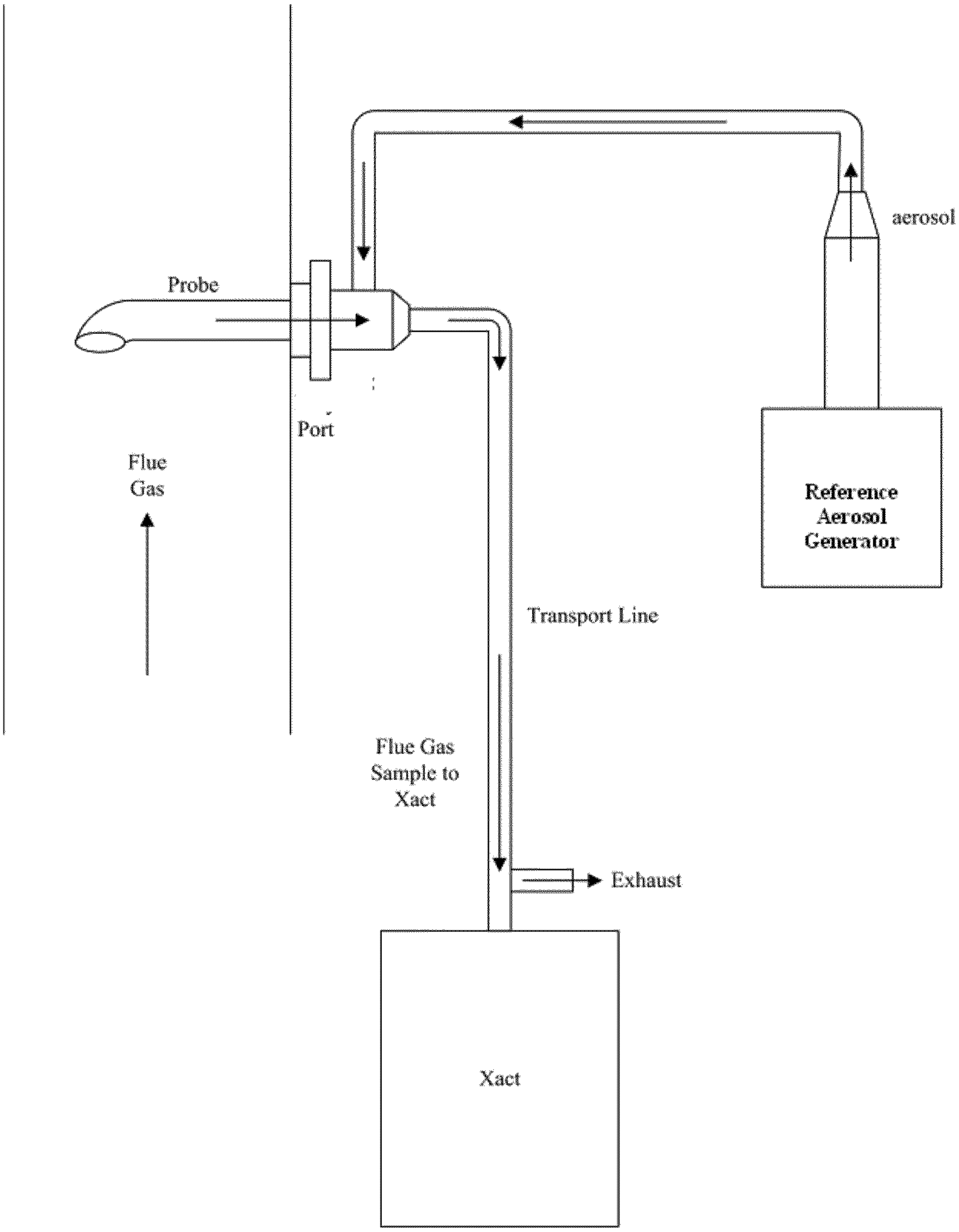

Figure 2. Diagram of Dynamic Spiking Protocol

5.0 Stability

5.1. Daily Flow Checks

The Xact has demonstrated its reliability with over five years of operation on a hazardous waste incinerator. Over the course of that time, the Xact demonstrated excellent measurement stability passing every quarterly audit and every annual RATA. Additionally the Xact demonstrated excellent stability on daily flow, zero and upscale XRF checks as well as excellent stability on the check of XRF stability that occurs with every sample. Figures 3 and 4 show the stability of the daily upscale and flow checks over the course of a year between March 2006 and March 2007.

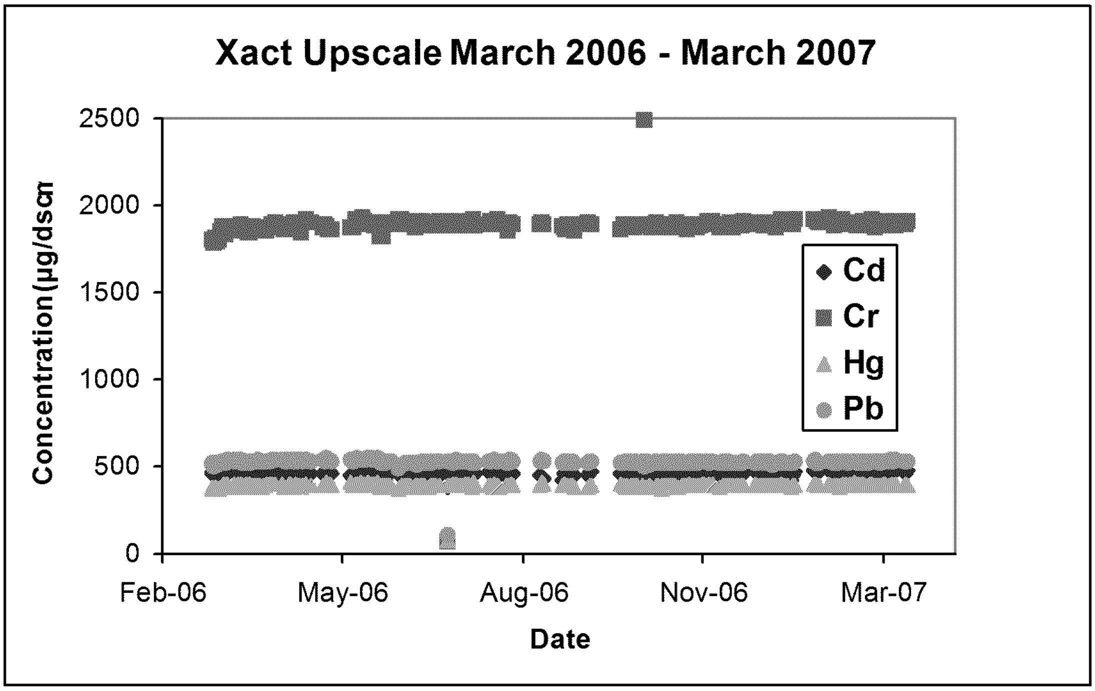

Figure 3. Xact Daily Upscale Stability Over the Course of a Year

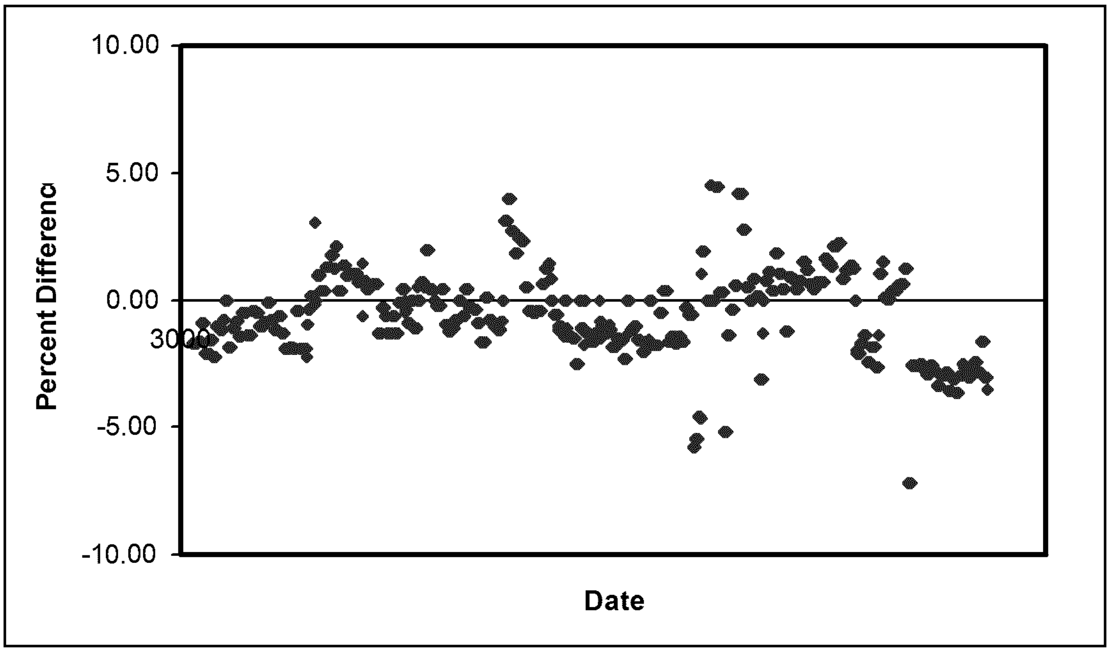

Figure 4. Daily Flow Stability over the Course of a Year

5.2. Quarterly Audits

The Xact was required under the hazardous waste incinerator's Alternative Monitoring Petition to have less than 10% error on quarterly audits for each regulated element (chromium, arsenic, cadmium, mercury and lead) and less than 10% flow error for each audit. Over the last five years the overall average XRF audit error was 1.6% while the overall average flow error was 1.8%. Table 1 shows the data for every flow and XRF audit for which data was available.

Table 1. Xact Flow and Audit Data

Audit Year	Quarter	Audit Date	Flow Error	XRF Audit Error				
				Cr	As	Cd	Hg	Pb
2007	1	3/1/2007	3.04%	1.46%	2.18%	2.84%	1.75%	2.34%
	2	5/25/2007	3.13%	3.32%	0.13%	4.23%	2.60%	2.96%
	3	8/29/2007	0.68%	-3.74%	2.18%	-4.13%	2.36%	2.76%
	4	12/26/2007	1.42%	6.50%	0.36%	7.36%	4.18%	0.40%
2008	1	2/15/2008	NA	0.22%	0.11%	1.20%	-0.99%	0.87%
	2	3/17/2008	1.07%	1.93%	0.66%	1.82%	2.16%	2.34%
	3	5/20/2008	0.53%	2.96%	2.61%	3.30%	2.53%	0.68%
	4	10/20/2008	1.37%	1.77%	0.72%	1.48%	0.56%	1.06%
2009	1	1/7/2009	2.10%	0.60%	2.94%	1.52%	3.45%	0.46%
	2	5/6/2009	3.67%	1.49%	4.09%	1.07%	1.78%	0.30%
	3	7/9/2009	0.84%	2.00%	5.43%	2.78%	0.72%	0.22%
	4	NA	NA	NA	NA	NA	NA	NA
2010	1	1/12/2010	NA	1.60%	5.13%	0.45%	0.71%	2.11%
	2	4/25/2010	NA	1.61%	5.92%	1.12%	4.00%	0.96%
	3	7/13/2010	1.68%	-3.47%	-0.92%	-2.82%	-2.42%	-2.11%
	4	12/10/2010	NA	2.00%	0.82%	2.70%	1.83%	2.91%
AVE			**1.77%**	**1.35%**	**2.16%**	**1.66%**	**1.68%**	**1.22%**

NA - Data Not Available

5.3. Annual Relative Accuracy Test Audits (RATA)

Annual relative accuracy test audits were also a part of the Xact's quality assurance procedures required by Eli Lilly's Alternative Monitoring Petition. These RATAs consisted of challenging the Xact with a reference aerosol containing each of the five metals regulated at the facilities (a description of this procedure can be found in Section 4.3 of this document). The reported Xact concentration was plotted against the reference aerosol concentration for each metal and the slope, intercept and correlation coefficient for each fit was determined. The Xact meet these criteria for each of the six RATAs performed. The slope of the best fit line for each of these RATAs can be found in Table 2.

Table 2. Xact RATA Results

Year	Slope					
	Cr	As	Cd	Hg	Pb	Average
2006	0.83	0.90	0.85	0.82	0.85	0.85
2006 (Quarterly)	0.91	0.77	0.95	0.92	0.93	0.89
2007	0.84	0.82	0.88	0.84	0.81	0.84
2008	0.96	0.71	0.98	0.99	0.97	0.92
2009	0.96	0.99	0.99	1.10	1.00	1.01
2010	0.97	1.06	1.11	1.02	1.04	1.04
Average	**0.91**	**0.87**	**0.96**	**0.95**	**0.93**	**0.93**

6.0 Source Types Sampled by the Xact

6.1. Overview

In addition to the testing that has taken place at a hazardous waste incinerator, the Xact has been tested at several different types of combustion facilities, including:

1. A US Army Demilitarization Furnace
2. A pilot scale coal combustion source
3. A full scale coal fired power plant

These facilities constitute a diverse range of fuel types, controls, stack temperatures and stack conditions. Table 3 summarizes the types of sources and some of the stack characteristics at those sources. More detail on each test is contained in Sections 6.2 to 6.4.

Table 3. Summary of Sampling Conditions for Xact Testing

Source Type	Fuel	Controls	Stack Temp (°F)	PM (µg/m³)	HCl (ppm)
Hazardous Waste Incinerator	Natural Gas	ESP and Wet Scrubber	120	8 to 16 mg/m³	10 ppm
Demilitarization Incinerator	Diesel Fuel	Baghouse	500	10 mg/m³	?
Pilot Scale Coal Combustor	Bituminous	ESP and Wet Scrubber	120	?	?
Coal Fired Power Plant	sub-bituminous	ESP	300	275	?

Many lead smelters are natural gas fired and operate with fabric filter (baghouse) controls. The Xact has demonstrated accurate measurement of lead on natural gas sources and on sources using baghouses.[11] ICR data from the four individual facilities available on the Docket as of 6/21/11 also indicates that typical PM concentrations downstream of controls at secondary lead smelters are around 1 to 2 mg/m³, significantly less challenging than the conditions in which the Xact has already demonstrated accurate measurement.[12,13,14,15] Finally typical lead smelter outlet temperatures range from about 300°F to 430°F. The Xact has demonstrated accurate lead measurement in conditions up to 500°F.

6.2. Pb Accuracy Testing at a Demilitarization Incinerator

In 2002, the Army Core of Engineers sponsored a study that compared the concentrations reported by the XCEM to that of Method 29. The XCEM was a prototype to the current Xact that utilized the same filter media and XRF analysis. This test was performed on a U.S. Army munitions demilitarization furnace in Toole, Utah. This facility burns diesel fuel and is equipped with a baghouse. Typical PM concentrations are around 10mg/dscm and the stack exit temperature is around 500°F.[16]

During testing, munitions were incinerated and metals solutions were then spiked into the emission stream downstream of the furnace. Concentrations of lead (Pb), and other metals were measured with paired Method 29 trains and with the XCEM at approximately the same location in the stack. Lead concentrations ranged from about 25 to 150 µg/dscm. Figure 5 shows a plot of the average reported XCEM concentration versus the average Method 29 lead concentration. The slope of the best fit line is 1.09, indicating excellent agreement between the XCEM and Method 29. The relative accuracy the XCEM was also calculated and found to be 4.4% again indicating excellent agreement between the XCEM and method 29.[16]

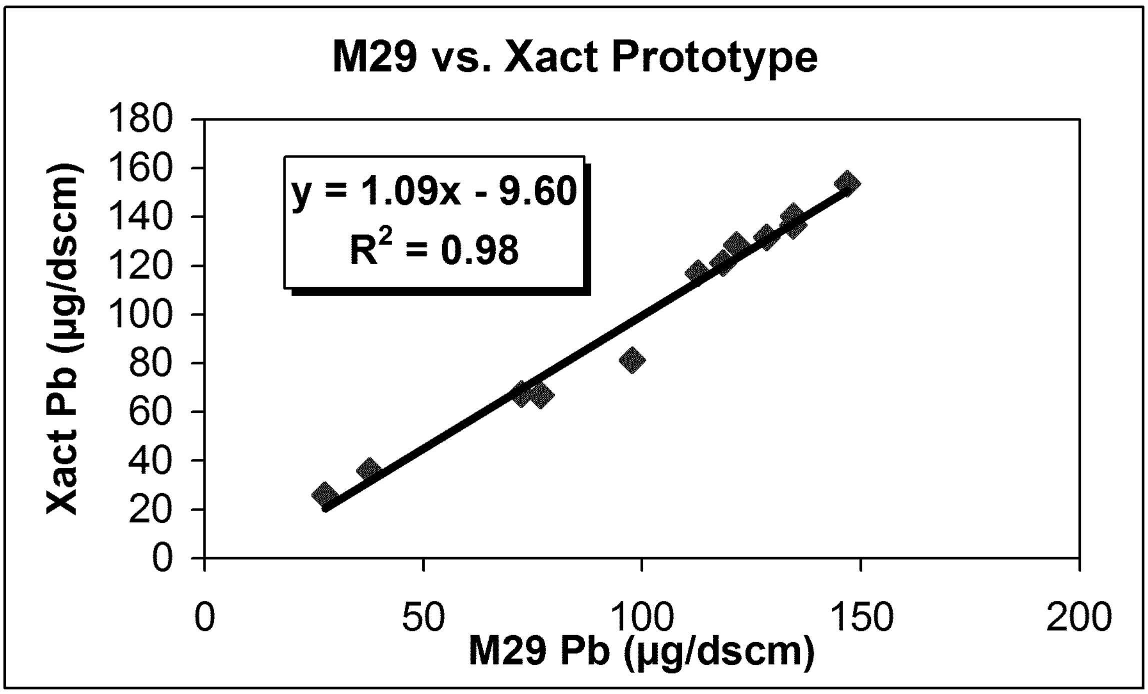

Figure 5. Comparison of Xact Prototype Versus M29.

6.3. Multi-metals on a Coal Fired Source

As part of a Small Business Innovative Research (SBIR) funded grant, the Xact participated in a test designed to determine the feasibility of using the instrument on coal fired incineration sources. This study took place at the US EPA's Multi-Pollution Control Research Facility (MPCRF), located in Research Triangle Park North Carolina. The MPCRF is a pilot-scale combustor operated by the Air Pollution Technology Branch (APTB) of the EPA's National Risk Management Research Laboratory. The MPCRF is able to fire pulverized coal, distillate oil, and/or natural gas at 4 million Btu/hr. The MPCRF is equipped with wet and dry flue gas cleaning systems and closely simulates full-scale emission sources. During this study the facility burned bituminous coal with ESP and wet scrubber controls. The Xact extracted a sample of stack effluent downstream of all controls. This extracted effluent was dynamically spiked with five different metals (chromium, arsenic, cadmium, mercury and lead) at three different concentration levels (27, 92, 250 μg/dscm) using a reference aerosol generator. These spiking procedures are identical to those performed on the hazardous waste incinerator and to those proposed as performance specifications and on-going quality assurance in appendices A and B of this document.

Figure 6 shows a plot of the Xact reported concentration versus the reference aerosol concentration. The slope of the best fit line shows a slope of 1.09 indicating excellent agreement between the reference aerosol and the Xact reported concentrations for all metals. Figure 7 shows the same plot, but for lead only. In this case the slope is 0.99, indicating nearly perfect agreement between the Xact reported lead concentration and the reference lead concentration.[17]

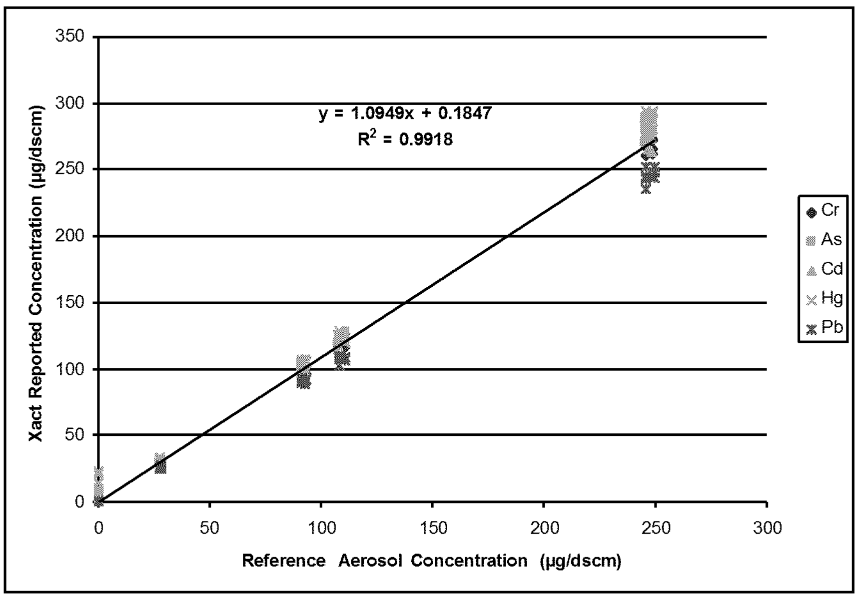

Figure 6. Xact Reported Concentrations versus Reference Aerosol Concentrations on a Coal-Fired Pilot Scale Source

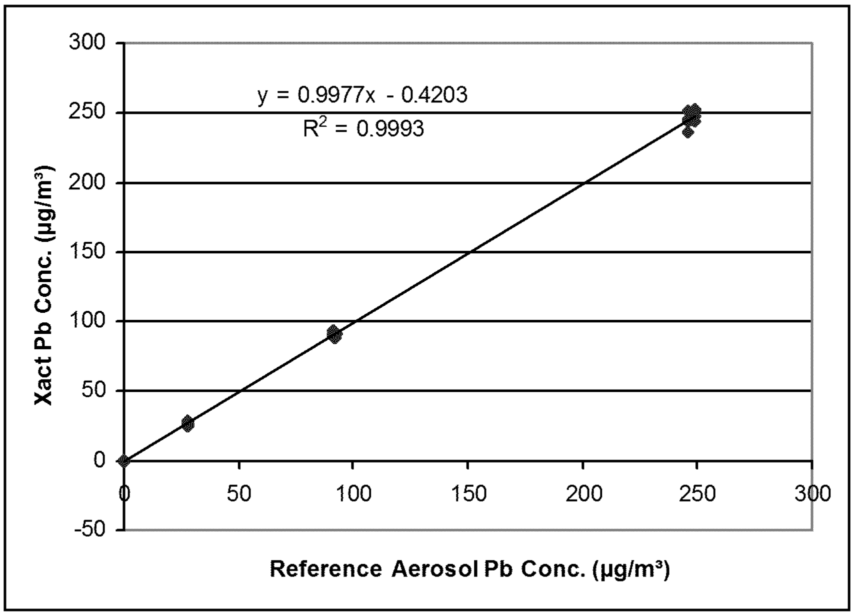

Figure 7. Xact Reported Pb Concentrations versus Reference Aerosol Pb Concentrations on a Pilot Scale Coal-Fired Source

6.4. Mercury at a Coal Fired Power Plant

The measurement accuracy of the Xact has also been tested on a full scale coal combustion source. In 2008, the Xact was deployed for several weeks at coal fired electric generating facility in the northwest. This facility is a 585 MW electric generating station burning pulverized coal and operating with electrostatic precipitator (ESP) controls. The Xact was deployed at the sampling level and operated there for three weeks. As part of the testing the Xact was compared against Method 30B under the procedures described by Performance Specification 12A. Figure 8 below shows the Xact test results for each measured point versus Method 30B. The Xact's relative accuracy for the test was 3.5%, which is well below the PS-12A criteria of 20%.[18,19] Although lead was not measured in this study, at the request of the host site, this study does demonstrate the ability of the Xact to make accurate measurements on a full scale coal combustion source.

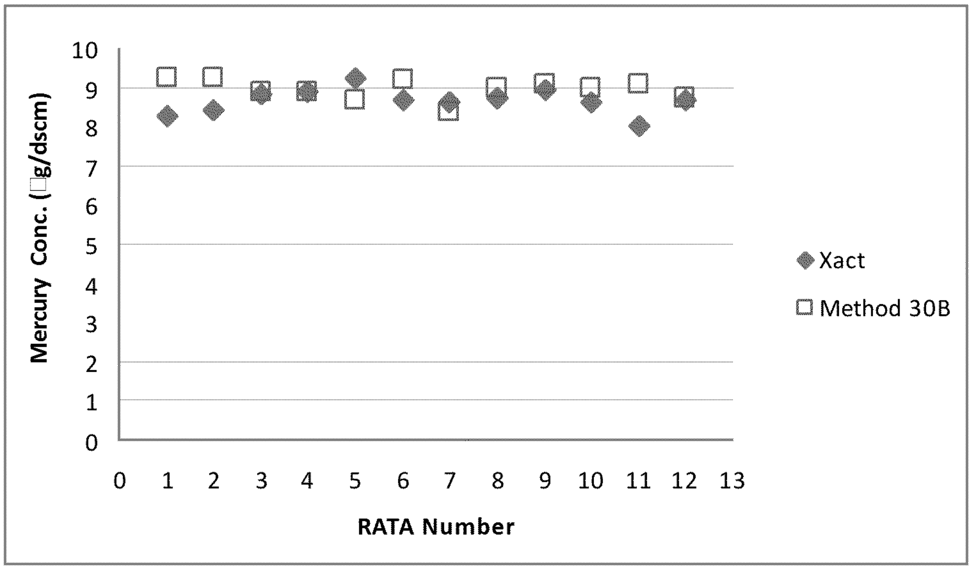

Figure 8. Xact Comparison With Method 30B

7.0 Measurement Range

The EPA has proposed a facility wide MACT standard for Pb emissions from secondary lead smelter stacks of 0.20 mg/dscm with an individual stack limit of 1 mg/dscm. The Xact has demonstrated linearity from its detection limit for lead of 0.0004 mg/m³ (with 15 minute sampling and analysis time) to an upper end of nearly 2 mg/m³. Since the highest recorded lead concentration in ICR test is 1.6 mg/m^3, the Xact's analytical range is more than adequate to meet the monitoring requirements of this industry. Sections 7.1 and 7.2 document how the Xact's measurement range was determined.

7.1. Testing to determine the upper limits

As part of developing its alternative monitoring petition, Eli Lilly performed a study to determine the upper limits of the Xact's quantitative range. During that study, the Xact was challenged at several concentration levels up to about 2500 µg/m³ using a reference aerosol. The Xact reported concentration was compared to the reference aerosol concentration, and a linear least squares fit was performed. Figure 9 shows the results for this linearity testing for lead.

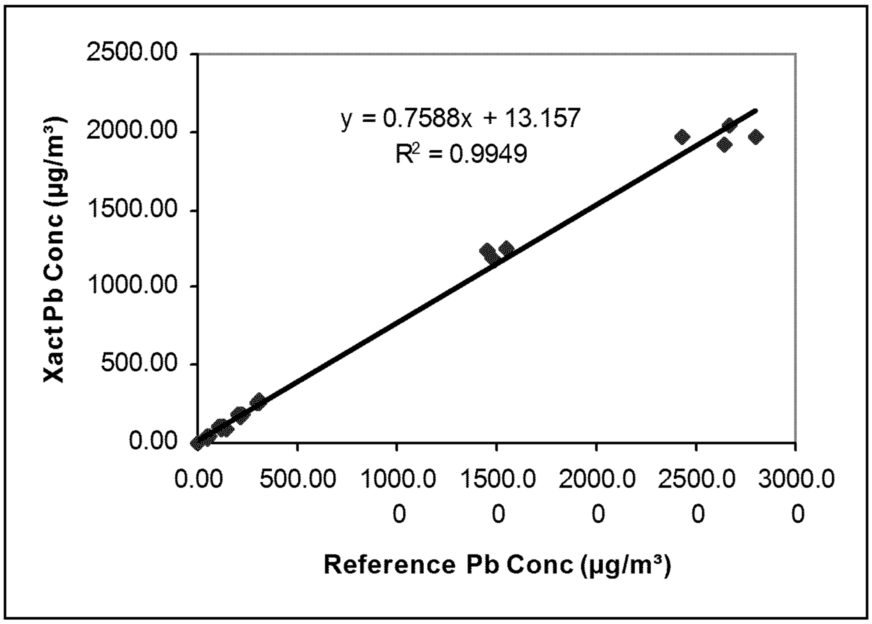

Figure 9. Lead Quantitative Range Testing.

7.2. Detection Limits

The Xact's detection limits for lead and several other metals were determined immediately after initial deployment on a hazardous waste incinerator. The detection limit represents the 95% confidence interference-free limit and is based on the analysis of 3899 individual blank samples. This represents one of the most rigorous determinations of a minimum detection limit for a continuous emissions monitor anywhere.

8.0 Conclusions

The EPA has specifically requested comments on whether it is feasible to monitor lead at secondary lead smelters with a CEMS, and the answer is emphatically yes! The Xact has demonstrated its accuracy, reliability, and stability for five years on a hazardous waste incinerator. It has also demonstrated measurement accuracy on a wide variety of sources encompassing a large range of fuel types, controls, and stack conditions, including conditions similar to those found on secondary lead smelters. Finally, the measurement range is more than adequate to meet the monitoring needs of secondary lead smelters. The performance specifications and on-going quality assurance procedures presented in appendices A and B are nearly identical to those used for years at Eli Lilly's hazardous waste incinerator. They supply a robust quality assurance and quality control regime that will ensure that emissions data collected from secondary lead smelters are accurate.

9.0 References

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Appendix A

Performance Specification ZZ. Specifications and Test Procedures for Lead Continuous Emissions Monitoring Systems on Stationary Sources.

1.0 Scope and Application

1.1. Analyte.

The analyte measured by these procedures and specifications is total lead (Pb) in concentrations of micrograms per standard cubic meter ($\mu g/m^3$).

1.2. Applicability

1.2.1. This specification is for evaluating the acceptability of Pb continuous emissions monitoring systems (CEMS) installed at stationary sources at the time of, or very soon after installation. The lead CEMS must be capable of measuring total Pb in $\mu g/m^3$ on a continuous basis regardless of speciation and record that data at standard conditions on a wet or dry basis.

1.2.2. This specification is not designed to evaluate an installed CEMS's performance over an extended period of time nor does it address calibration techniques or procedures specific to each CEMS manufacturer. The source owner is required to calibrate, maintain and operate the CEMS properly. The Administrator may require, under Section 114 of the Clean Air Act, the operator to conduct performance evaluations at other times besides the initial performance evaluation test.

2.0 Summary of Performance Specification

Procedures for determining the relative accuracy, linearity, and calibration drift are outlined. Additionally CEMS installation and measurement location specifications, and performance criteria are included.

3.0 Definitions

3.1. Lead (Pb) CEMS

The total equipment required to measure lead in stack or duct effluent. Major systems in a lead CEMS may include the probe and transport line, the analyzer, the flow system, and the data recorder.

3.2. Analyzer

The portion of the lead CEMS that identifies Pb and measures its mass.

3.3. Flow System

If a lead CEMS is an extractive type and the flow or volume measurement is used in the calculation of total Pb concentrations, the flow system consists of all the components required to withdraw, treat, measure and control the flow. These components may include, but are not necessarily limited to the following: pump, dryer, flow sensor, and control valve.

3.4. Reference Aerosol Generator

A reference aerosol generator produces an aerosol by nebulizing a solution of known concentration at a measured rate into a measured carrier gas flow to emit an aerosol at a known concentration that is traceable to NIST standards.

3.5. Upscale Drift Standard

The reference material used to challenge the upscale measurement stability of a Pb CEMS.

3.6. Zero Drift Standard

The reference material used to challenge the low or blank measurement stability of a Pb CEMS.

3.7. Emission Limit

This is the maximum lead (Pb) emission concentration allowed under the applicable regulation.

3.8. Dynamic Spiking

A procedure used to determine the accuracy, precision and bias of a monitoring system by quantitatively spiking a certified gas or aerosol into a pollutant gas stream.

3.9. Upscale Drift

The difference between the expected upscale response to a reference standard and the actual response of the Pb CEMS expressed as a percentage of the emission limit.

3.10. Zero Drift

The difference between the expected zero response to a reference standard and the actual response of the Pb CEMS expressed as a percentage of the emission limit.

3.11. Flow Drift Check

A procedure to check the stability of the Pb CEMS sample flow rate against the flow rate as measured by a quality assurance flow meter.

3.12. Flow Drift

The difference between the flow as measured by the Pb CEMS primary flow meter and a quality assurance flow meter expressed as a percentage of the quality assurance flow meter.

3.13. Flow Audit

A procedure to check the flow of the Pb CEMS sample flow rate against the flow rate as measured by NIST traceable reference flow meter.

3.14. Flow Calibration Error

The difference between the flow as measured by the Pb CEMS primary flow meter and a quality assurance flow meter expressed as a percentage of the quality assurance flow meter.

3.15. Analyzer Audit Standard

A standard with a known concentration or mass of lead that is NIST traceable or traceable to NIST standards.

3.16. Analyzer Calibration Audit

The procedure by which a Pb CEMS's response to the analyzer audit standard is compared to the certified concentration or mass of that standard.

3.17. Analyzer Calibration Error

The difference between the Pb CEMS analyzer's response to the analyzer audit standard and that standard's certified value expressed as a percentage of the certified value.

3.18. Linearity Accuracy Audit

A test used to evaluate the accuracy and precision of the Pb CEMS over a range of concentrations. The audit is performed by dynamically spiking the Pb CEMS transport line with aerosols of known lead concentrations.

4.0 Interferences [Reserved]

5.0 Safety

The procedures required under this performance specification may involve hazardous materials, operations, and equipment. This performance specification may not address all of the safety problems associated with these procedures. It is the responsibility of the user to establish the appropriate safety and health practices and determine the applicable regulatory limitations prior to performing these procedures. Please consult the CEMS manufacturer or appropriate reference material manufacturer for proper safety procedures.

6.0 Equipment and Supplies

6.1. CEMS Equipment Specifications

6.1.1. Data Recorder

The Pb CEMS must have a data recorder with an output range that includes the full range of the expected lead concentration values.

6.1.2. Quality Assurance Equipment

The Pb analyzer must be equipped with an upscale and zero standard to check the upscale and zero drifts respectively, on an automatic basis. In addition, for the analyzer audit, a NIST traceable or traceable-to-NIST lead analyzer audit standard is required.

If the Pb CEMS is an extractive type that measures the sample volume and uses that measured volume in the calculation of the output value of the CEMS, the lead CEMS needs to be equipped with a quality assurance flow meter. This meter must allow the CEMS to check the primary flow measurement automatically on a daily basis. In addition a NIST traceable flow meter is required to check the accuracy of the CEMS primary flow meter as part of the flow audit

6.1.3. Reference Aerosol Delivery System

The Pb CEMS must allow for the introduction of a reference Pb aerosol at a point as close to the probe tip as possible.

6.2. Other Equipment and Supplies

Other equipment or supplies may be necessary to perform the procedures found in this document. Please check with your CEMS manufacturer.

7.0 Reagents and Standards

7.1. Upscale Drift Standard

Each Pb CEMS must be equipped with a lead (Pb) upscale drift standard. This standard must allow for automated daily checks of the analyzer portion of the Pb CEMS. The expected response from this standard should be greater than 80 percent of the emission limit.

7.2. Zero Drift Standard

Each Pb CEMS must be equipped with a zero drift standard. This standard must allow for automated daily checks of the analyzer portion of the Pb CEMS. The expected response from this standard should be less than 20 percent of emission limit.

7.3. Quality Assurance Flow Meter

If your Pb CEMS is an extractive type that measures the sample volume and uses the measured sample volume as part of calculating the output value your CEMS must be able to check the sample flow rate to verify the precision of the flow measurement equipment. The flow check must be able to be performed automatically on a daily basis.

7.4. Analyzer Audit Standard

A standard with a known concentration or mass of lead that is NIST traceable or traceable to NIST standards.

7.5. Flow Audit Reference Flow Meter

If your Pb CEMS is an extractive type that measures the sample volume and uses the measured sample volume as part of calculating the output value of your CEMS you must have a NIST traceable reference flow meter to verify the accuracy of the flow measurement equipment. The reference flow meter must be within its certification period and be able to measure flow in the units used by the Pb CEMS.

7.6. Reference Aerosol Generator

A reference aerosol generator is needed to perform the linearity audit. It must be capable of generating a range of Pb concentrations up to and including the emission limit specified in the applicable regulation.

8.0 Performance Specification Test Procedures

8.1. Installation and Measurement Location Specifications

8.1.1. CEMS Installation

Install the Pb CEMS at an accessible location downstream of all pollution control equipment. Place the probe inlet or any other sampling interface at a location in the stack or vent that is representative of the stack gas concentration of Pb. If the Pb CEMS samples from a single point within the stack or duct, that location should be free from stratification of Pb. Locations likely to meet these criteria are given in sections 8.1.2 and 8.1.3.

8.1.2. Measurement Location

The measurement location should be 1) at least two equivalent diameters downstream of the nearest pollution control device, point of pollution generation, or other point at which a change of pollutant concentration may occur and 2) at least half a diameter upstream from the pollutant exhaust. The equivalent duct diameter is calculated according to Method 1 in appendix A-1 of CFR Part 60.[1]

8.1.3. Pb CEMS Sample Extraction Point

Use a sample extraction point that is either 1) no less than 1.0 meters from the stack or duct wall, or 2) within the centroidal velocity traverse area of the stack. This does not apply to cross stack or in situ Pb CEMS.

8.2. Seven-Day Calibration Drift Check

8.2.1. Calibration Drift Test Period

While the affected facility is operating normally, or as specified in an applicable regulation, determine the magnitude of the zero drift, the upscale drift and the flow drift, one at least one time per day for seven consecutive unit operating days. The seven consecutive unit operating days need not be seven consecutive calendar days.

8.2.2. Purpose

The purpose of the calibration drift checks is to determine the stability of the analyzer and flow system portions of the Pb CEMS. If your Pb CEMS is not an extractive type of CEMS and does not use a flow measurement to determine Pb concentrations than the flow calibration drift check is not required.

8.2.3. Zero Drift Check

Challenge the Pb CEMS with a zero standard and calculate the zero drift by dividing the difference between the zero drift standard value (*R*) and the Pb CEMS response (*A*) to the zero drift standard by the applicable emission limit (*L*) (Equation 1).

8.2.4. Upscale Drift Check

Challenge the Pb CEMS with the upscale standard and calculate the upscale drift by dividing the difference between upscale drift value (*R*) and the Pb CEMS response (*A*) by the applicable emission limit (*L*) (Equation 1).

8.2.5. Calculation of Upscale and Zero Drift Checks

Both the upscale and zero drift are calculated according to Equation 1 below.

$$CD = \frac{|R - A|}{L} x100 \qquad \text{Equation 1}$$

Where:

CD = Either the upscale or zero calibration drift check.

R = Either the upscale or zero standard reference value

A = Either the Pb CEMS response to the upscale or zero standard

L = The emission limit expressed in the μg/m³

8.2.6. Flow Drift Check

If your Pb CEMS is an extractive type that uses a flow or volume measurement to determine the Pb concentration, a flow drift check must be performed at least once each day. During this flow drift check, the flow as measured by CEMS's primary flow or volume measurement device is compared to a secondary quality assurance flow measurement device that is used exclusively for the purpose of performing the flow drift check. The flow calibration drift is calculated according to Equation 2. The flow rate during the flow check must be the same as during normal sampling. The sample flow check may be performed over a time period shorter than the normal Pb CEMS sampling interval.

$$FD = \frac{|F_P - F_{QA}|}{F_{QA}} x100 \qquad \text{Equation 2}$$

Where:

FD = The flow drift as a percentage of the flow measured by the quality assurance flow meter.

F_p = The flow as measured by the primary flow measurement device in the Pb CEMS

F_{QA} = The flow as measured by the CEMS's secondary quality assurance flow meter.

8.3. Calibration Audits

8.3.1. Analyzer Calibration Audit

The analyzer portion of each Pb CEMS must be challenged with a NIST traceable or traceable-to-NIST standard for Pb. The analyzer calibration error (*AE*) is calculated by dividing the difference between the known concentration of the Pb audit standard (C_s) and the concentration reported by the Pb CEMS (C_c) by the known concentration of the Pb audit standard (Equation 3).

$$AE = \frac{|C_S - C_c|}{C_s} x100 \qquad \text{Equation 3}$$

8.3.2. Flow Calibration Audit

If your Pb CEMS is an extractive type that measures flow or volume and utilizes that flow or volume measurement as part of calculating the output value you must perform a flow calibration audit to determine the flow calibration error. During this procedure you must compare the Pb CEMS measured flow rate to the flow rate as measured by a NIST traceable reference flow meter. The flow rate during the audit must be the same as that used during normal instrument sampling. You must make at least three measurements of flow on both the Pb CEMS and the reference flow meter. For each measurement set, calculate the flow calibration error (*FE*) by dividing the difference between the flow as measured by the reference flow meter (F_s) and the flow as measured by the Pb CEMS (F_c) by the reference flow meter (Equation 4). Then calculate the average error for each of the three measurements.

$$FE = \frac{|F_S - F_c|}{F_s} x100 \qquad \text{Equation 4}$$

8.4. Linearity Accuracy Audit

The linear accuracy audit is a dynamic spiking procedure in which the lead CEMS is challenged with a reference aerosol containing lead at several different concentration levels. The aerosol concentrations are produced using a Reference Aerosol Generator (RAG) and are introduced into the Pb CEMS transport line while it is sampling stack effluent. The concentrations reported by the CEMS are plotted against concentrations generated using a reference aerosol generator and a best fit linear regression curve is generated. The slope of this line is an indication of the accuracy of the Pb CEMS over a range of concentrations, while the correlation coefficient is an indicator of instrument precision. Sections 8.4.1 to 8.4.8 describe procedures for the linear accuracy audit.

8.4.1. Spiking Location

The Pb reference aerosol must be introduced into the Pb CEMS transport line at a point as close to the probe tip as possible. In this way the entire Pb CEMS including, the transport line, flow system, analyzer and data recorder are challenged.

8.4.2. Reference Aerosol Generator

The reference aerosol generator used for the linear accuracy audit must comply with the specifications and procedures laid out in the Traceability Protocol for Certification of Reference Aerosol Generators.[2] This means that the expanded uncertainty in the concentration of the reference lead aerosol must not exceed 10%.

8.4.3. Transport Line Flow Measurement

The linear accuracy audit is a dynamic spiking procedure, meaning that the lead containing aerosol is introduced into the stack effluent sampled by the Pb CEMS. For this reason the total flow (sampled stack gas and reference aerosol) in the Pb CEMS transport line must be measured to determine the concentration of lead being sampled by the CEMS. Flow in the transport line may be measured in several ways. This procedure outlines two approaches: laminar flow elements and flow by dilution.

8.4.3.1. Laminar Flow

Prior to spiking, a calibrated laminar flow element may be inserted into the Pb CEMS's transport line downstream of all instrument sampling. The measured flow from the laminar flow element may be used to calculate the lead concentration being sampled by the Pb CEMS.

8.4.3.2. Flow by Dilution

Flow by dilution is a method of measuring flow where a concentration of a gas is quantitatively introduced into the flue gas stream and measured down stream by a calibrated instrument. For instance, a known concentration of propane can be quantitatively introduced into the flue gas stream and the diluted propane measured downstream using a gas chromatograph (GC). The calibration gas must be introduced into the gas stream quantitatively. Typically this is done by using a mass flow controller.

Prior to spiking, the gas chromatograph or other measurement instrumentation must be calibrated at least three points through the expected measurement range. After the dynamic spiking procedure is completed the measurement instrument should be checked for bias at each of the four measurement points. The bias should be less than 5% of the expected value for each point.

The transport line flow (F_T) is related to the concentration of the spiked gas (G_s), flow rate of the spiked gas (F_s) and the measured gas concentration (G_M) using the following relationship (Equation 5).

$$F_T = \frac{G_s}{G_M} F_S \qquad \text{Equation 5}$$

8.4.3.3. Calculation of the Reference Lead Concentration

The reference aerosol generator (RAG) creates an aerosol of a known concentration which is then introduced into the Pb CEMS transport line which has a measured flow rate (Section 8.4.3.2). The concentration of lead produced by the RAG is therefore, diluted by the stack gas flow. This diluted concentration is the reference concentration then that should be measured by the Pb CEMS. This reference concentration (C_R) is calculated by multiplying the RAG produced aerosol concentration (C_{RAG}) by the ratio of the reference aerosol generator flow (F_{RAG}) to the total flow as measured (F_T) according to the procedures in Section 8.4.3.2 (Equation 6).

$$C_R = \frac{F_{RAG}}{F_T} C_{RAG} \qquad \text{Equation 6}$$

8.4.4. Source Operation During Spiking

The linear accuracy audit procedures require that the background concentrations of lead be less than 15% of the applicable emission limit during the testing period. Therefore the source should be operated in a manner to prevent any lead emissions in excess of 15% of the emission limit (e.g. only burn natural gas). If this is not possible or if background concentrations of lead still exceed 15% of the emission limit even after taking reasonable steps to eliminate lead from the effluent emissions, it may be necessary to filter lead from the transport line upstream of the spiking location (e.g. use a particulate filter upstream of the spiking location).

8.4.5. Determination of Background Lead Concentrations

Prior to spiking, determine the background concentration of lead as measured by Pb CEMS by taking nine measurements while the unit is operating in the manner described in Section 8.4.4. If necessary this background concentration of lead may be subtracted from the total lead as measured by the CEMS during spiking.

8.4.6. Pb CEMS Operation

The Pb CEMS must be operated normally throughout the course of the spiking procedures. This includes operating at normal flow rates and maintaining sampling times that are the same as those used during normal instrument operation.

8.4.7. Spiking Procedures

The instrument must be challenged at three different lead concentration levels as listed below:

1. Low – 10 to 30 percent of the emission limit
2. Mid - 40 to 60 percent of the emission limit
3. High – 80 to 120 percent of the emission limit

You may spike at more concentration levels and include them in the regression analysis if, for example, you want to demonstrate a higher instrument span.

At least nine valid measurements must be acquired at each concentration level. The first two measurements at each concentration level may be eliminated to allow for time for the reference aerosol concentration to stabilize.

8.4.8. Linear Least Squares Regression Analysis

Plot each Pb CEMS reported concentration against the reference lead concentration (C_R from Equation 6) and determine the slope, intercept and correlation coefficient of the best fit line. This best fit line will have the form as shown in Equation 7. The slope, intercept and correlation coefficient may be calculated according to Equations 8, 9 and 10 respectively.

$$\hat{y} = b_o + b_1 x \qquad \text{Equation 7}$$

Where:

$\hat{y}$ = Concentration output of the Pb CEMS as predicted by the linear least squares fit

b_1 = The slope of the best fit line

b_o = The intercept of the best fit line

x = The reference aerosol

$$b_1 = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^{n}(x_i - \bar{x})^2} \qquad \text{Equation 8}$$

Where:

b_1 = The slope of the best fit line

x_i = An individual reference aerosol Pb concentration

$\bar{x}$ = The average reference aerosol Pb concentration

y_i = An individual reported Pb CEMS concentration

$\bar{y}$ = The average reported Pb CEMS concentration

$$b_o = \bar{y} - b_1\bar{x} \qquad \text{Equation 9}$$

Where:

b_1 = The slope of the best fit line

b_o = The intercept of the best fit line

$\bar{y}$ = The average reported Pb CEMS concentration

$\bar{x}$ = The average reference aerosol Pb concentration

$$r = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \sum_{i=1}^{n}(y_i - \bar{y})^2}} \qquad \text{Equation 10}$$

Where:

r = The correlation coefficient

x_i = An individual reference aerosol Pb concentration

$\bar{x}$ = The average reference aerosol Pb concentration

y_i = An individual reported Pb CEMS concentration

$\bar{y}$ = The average reported Pb CEMS concentration

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure [Reserved]

12.0 Calculations and Data Analysis [Reserved]

13.0 Method Performance

13.1. Zero Drift Criteria

The zero drift must be less than 20% of the emission limit every day for seven consecutive unit operating days.

13.2. Upscale Drift Criteria

The upscale drift must be less than 15% of the emission limit every day for seven consecutive unit operating days.

13.3. Flow Drift Criteria

The flow drift must be less than 15% of the flow as measured by the Pb CEMS quality assurance flow meter every day for seven consecutive unit operating days.

13.4. Analyzer Calibration Error

When the analyzer calibration audit standard is analyzed the concentration of lead as reported by the Pb CEMS must be within 10% of the certified value of the analyzer audit standard.

13.5. Flow Calibration Error

When the unit is operating at normal flow rates, the average flow as measured by the Pb CEMS flow meter must be within 10% of the flow as measured by a NIST traceable reference flow meter.

13.6. Linear Accuracy Audit Criteria

Plot the Pb CEMS reported concentration versus the reference aerosol concentration. If the slope of the best fit line is between 0.85 and 1.15, the intercept is less than 20% of the emission limit, and the correlation coefficient is greater than 0.90, the Pb CEMS may be used without applying a correction factor. However, if the slope or intercept criteria fall outside of this range, a correction factor may be applied to the Pb CEMS data provided the following three criteria are met.

1. The slope of the best fit line is not greater than 1.30 or less than 0.70.

2. The intercept is not greater than 40% of the emission limit

3. The correlation coefficient is greater than 0.90.

If both the slope and intercept need to be adjusted the concentration reported by the Pb CEMS may be adjusted using Equation 11.

$$C_c = \frac{C_U - b_0}{b_1} \qquad \text{Equation 11}$$

The slope may be adjusted using Equation 12.

$$C_C = \frac{C_U}{b_1} \qquad \text{Equation 12}$$

The intercept may be adjusted using Equation 13.

$$C_C = C_U - b_o \qquad \text{Equation 13}$$

For all three equations

C_C = The corrected Pb CEMS concentration (µg/m³)

C_U = The uncorrected Pb CEMS concentration (µg/m³)

b_0 = The intercept of the best fit line

b_1 = The slope of the best fit line

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures [Reserved]

17.0 Bibliography

1. United States. Environmental Protection Agency [EPA]. Technology Transfer Network. Emission Measurement Center. Promulgated Methods. Method 1: Sample and Velocity Traverses for Stationary Sources. Washington, DC: EPA; 2004. Available: http://www.epa.gov/ttn/emc/promgate/m-01.pdf via the Internet. Accessed June 17, 2011.

2. Siemers, A.; Petterson, K.A.; Cooper, J.A.; Barth, D.; *Draft Traceability Protocol for Certification of Reference Aerosol Generators.*; EPA Contract EP-D-05-096. April, 2011.

18.0 Tables and Figures

Table 1. Initial Performance Tests and Test Criteria

Test Category	Test	Test Requirements	Test Criteria
Seven Day Calibration Drift Check	Zero Drift	Monitor zero standard for 7 consecutive days under normal operating conditions	< 20% drift every day for seven consecutive days
	Upscale Drift	Monitor upscale standard for 7 consecutive days under normal operating conditions	< 15% drift every day for seven consecutive days
	Flow Drift	Monitor flow drift for 7 consecutive days under normal operating conditions	< 15% drift every day for seven consecutive days
Calibration Audits	Analyzer Calibration Audit	Test a Pb standard designed to challenge the analyzer portion of the Pb CEMS	< 10% drift
	Flow Calibration Audit	Check the flow or volume measurement of the Pb CEMS using a reference flow measurement device	<10% Difference between the flow measurement device and the CEMS measured flow
Accuracy	Linearity Audit	❑ Use a Reference Aerosol Containing a known concentration of Pb ❑ Dynamically Spike the stack gas sampled by the Pb CEMS ❑ Need at least 3 concentration levels ❑ Also include a zero or background concentration with no spiking. ❑ Spike into source, or spike into transport line as close as possible to the probe	❑ Slope = 0.85 to 1.15 ❑ $r \geq 0.90$ ❑ intercept < 20% of emission limit ❑ if the above criteria are met then no correction ❑ if not met a correction may be applied in certain instances

Appendix B

Procedure W. Quality Assurance Requirements for Lead Continuous Emissions Monitoring Systems Used for Compliance Determination at Stationary Sources

1.0 Purpose and Application

1.1. Purpose

The purpose of Procedure W is to define the on-going quality control and assurance requirements for lead (Pb) continuous emissions monitors (CEMS). Adherence to the procedures in this document will assure the data integrity and accuracy of Pb CEMS results. Additionally, Procedure W contains reporting requirements and procedures for demonstrating that out of control Pb CEMS have been repaired and are producing accurate data. Initial performance requirements for Pb CEMS may be found in *Performance Specification ZZ. Specifications and Test Procedures for Lead Continuous Emissions Monitoring Systems on Stationary Sources.*[1] Pb CEMS meeting the performance criteria found in Procedure W and Performance Specification ZZ may be used by regulating agencies for compliance monitoring.

1.2. Applicability

1.2.1. Analytes

Procedure W covers the measurement of total lead (Pb) in stationary sources on a wet or dry basis.

1.2.2. Additional Quality Control and Assurance Requirements

Procedure W specifies the minimum requirements for controlling and assessing the quality of a Pb CEMS. Operators are encouraged to develop and implement more extensive quality assurance programs and to continue such programs where they already exist.

2.0 Definitions

2.1. Lead (Pb) CEMS

The total equipment required to measure lead in stack or duct effluent. Major systems in a lead CEMS may include the probe and transport line, the analyzer, the flow system, and the data recorder.

2.2. Analyzer

The portion of the lead CEMS that identifies Pb and measures its mass.

2.3. Flow System

If a lead CEMS is an extractive type and the flow or volume measurement is used in the calculation of total Pb concentrations, the flow system consists of all the components required to withdraw, treat, measure and control the flow. These components may include, but are not necessarily limited to the following: pump, dryer, flow sensor, and control valve.

2.4. Reference Aerosol Generator

A reference aerosol generator produces an aerosol by nebulizing a solution of known concentration at a measured rate into a measured carrier gas flow to emit a known aerosol concentration that is traceable to NIST standards.

2.5. Upscale Drift Standard

The reference material used to challenge the upscale measurement stability of a Pb CEMS.

2.6. Zero Drift Standard

The reference material used to challenge the low or blank measurement stability of a Pb CEMS.

2.7. Emission Limit

This is the maximum lead (Pb) emission concentration allowed under the applicable regulations.

2.8. Dynamic Spiking

A procedure used to determine the accuracy, precision and bias of a monitoring system by quantitatively spiking a certified gas or aerosol into a pollutant gas stream.

2.9. Upscale Drift

The difference between the expected upscale response to a reference standard and the actual response of the Pb CEMS expressed as a percentage of the emission limit.

2.10. Zero Drift

The difference between the expected zero response to a reference standard and the actual response of the Pb CEMS expressed as a percentage of the emission limit.

2.11. Flow Drift Check

A procedure to check the stability of the Pb CEMS sample flow rate against the flow rate as measured by a quality assurance flow meter.

2.12. Flow Drift

The difference between the flow as measured by the Pb CEMS primary flow meter and a quality assurance flow meter expressed as a percentage of the quality assurance flow meter.

2.13. Flow Audit

A procedure to check the flow of the Pb CEMS sample flow rate against the flow rate as measured by NIST traceable reference flow meter.

2.14. Flow Calibration Error

The difference between the flow as measured by the Pb CEMS primary flow meter and a quality assurance flow meter expressed as a percentage of the quality assurance flow meter.

2.15. Analyzer Audit Standard

A NIST traceable or traceable to NIST standard that can be used to challenge the analyzer portion of the Pb CEMS with a known mass or concentration of Pb.

2.16. Analyzer Calibration Audit

The procedure by which a Pb CEMS's response to NIST traceable or traceable to NIST lead standard is compared to the certified value of that standard.

2.17. Analyzer Calibration Error

The difference between the Pb CEMS analyzer's response to a NIST traceable or traceable-to-NIST certified value and that standards certified value expressed as a percentage of the certified value.

2.18. Linearity Accuracy Audit

A test used to evaluate the accuracy and precision of the Pb CEMS over a range of concentrations. The audit is performed by dynamically spiking the Pb CEMS transport line with aerosols of known lead concentration.

3.0 Interferences [Reserved]

4.0 Safety

The procedures required by Procedure W may involve hazardous materials, operations, and equipment. This performance specification may not address all of the safety problems associated with these procedures. It is the responsibility of the user to establish the appropriate safety and health practices and determine the applicable regulatory limitations prior to performing these procedures. Please consult the CEMS manufacturer or appropriate reference material manufacturer for proper safety procedures.

5.0 Equipment and Supplies

5.1. CEMS Equipment Specifications

5.1.1. Data Recorder

The Pb CEMS must have a data recorder with an output range that includes the full range of the expected lead concentration values.

5.1.2. Quality Assurance Equipment

The Pb analyzer must be equipped with an upscale and zero standard to check the upscale and zero drifts respectively, on an automatic basis. In addition, for the analyzer audit, a NIST traceable or traceable-to-NIST lead analyzer audit standard is required.

If the Pb CEMS is an extractive type that measures the sample volume and uses that measured volume in the calculation of the output value of the CEMS, the lead CEMS needs to be equipped with a quality assurance flow meter. This meter must allow the CEMS to check the primary flow measurement automatically on a daily basis. In addition a NIST traceable flow meter is required to check the accuracy of the CEMS primary flow meter as part of the flow audit

5.1.3. Reference Aerosol Delivery System

The Pb CEMS must allow for the introduction of a reference Pb aerosol at a point as close to the probe tip as possible.

5.2. Other Equipment and Supplies

Other equipment or supplies may be necessary to perform the procedures found in this document. Please check with your CEMS manufacturer.

6.0 Reagents and Standards

6.1. Upscale Drift Standard

Each Pb CEMS must be equipped with a lead (Pb) upscale drift standard. This standard must allow for automated daily checks of the analyzer portion of the Pb CEMS. The expected response from this standard should be greater than 80 percent of the emission limit.

6.2. Zero Drift Standard

Each Pb CEMS must be equipped with a zero drift standard. This standard must allow for automated daily checks of the analyzer portion of the Pb CEMS. The expected response from this standard should be less than 20 percent of emission limit.

6.3. Quality Assurance Flow Meter

If your Pb CEMS is an extractive type that measures the sample volume and uses the measured sample volume as part of calculating the output value your CEMS must be able to check the sample flow rate to verify the precision of the flow measurement equipment. The flow check must be able to be performed automatically on a daily basis.

6.4. Analyzer Audit Standard

A standard with a known concentration or mass of lead that is NIST traceable or traceable to NIST standards.

6.5. Flow Audit Reference Flow Meter

If your Pb CEMS is an extractive type that measures the sample volume and uses the measured sample volume as part of calculating the output value of your CEMS, you must have a NIST traceable reference flow meter to verify the accuracy of the flow measurement equipment. The reference flow meter must be within its certification period and be able to measure flow in the units used by the Pb CEMS.

6.6. Reference Aerosol Generator

A reference aerosol generator is needed to perform the linearity audit. It must be capable of generating a range of Pb concentrations up to and including the emission limit specified in the applicable regulation.

7.0 Quality Control Requirements

Each source owner or operator must develop and implement a quality control (QC) program. At a minimum, each QC program must include written procedures which should describe in detail, complete, step by step procedures and operations for all quality control activities. These activities include:

1. Daily zero, upscale and flow (if applicable) drift checks
2. Procedures for determining the zero, upscale and flow drift and methods of adjusting your Pb CEMS in response to the results of these drift checks.
3. Quarterly Audits including the Analyzer Audit and the Flow Audit (if applicable)

4. Routine and preventative maintenance procedures for the Pb CEMS (including a spare parts inventory).
5. Procedures for performing annual linear accuracy audits and procedures for adjusting your Pb CEMS results on the basis of linear accuracy audit results.
6. Data recording, calculations and reporting
7. A program of corrective action for malfunctioning Pb CEMS.

These written procedures must be kept on record and available for inspection by the responsible enforcement agency for the lifetime of the Pb CEMS or until you are no longer subject to the requirements of this procedure.

8.0 Calibration Drift Check and Audit Procedures

8.1. Calibration Drift Check

8.1.1. Frequency Requirements

Source owner and operators of Pb CEMS must check, record, and quantify the zero drift, the upscale drift and the flow drift (if applicable) at least once daily (approximately every 24 hours) in accordance with the procedures prescribed by the manufacturer.

8.1.2. Zero Drift

Challenge the Pb CEMS with a zero standard and calculate the zero drift by dividing the difference between the zero drift standard value (R) and the Pb CEMS response (A) to the zero drift standard by the applicable emission limit (L) (Equation 1).

8.1.3. Upscale Drift

Challenge the Pb CEMS with the upscale standard and calculate the upscale drift by dividing the difference between upscale drift value (R) and the Pb CEMS response (A) by the applicable emission limit (L) (Equation 1).

$$CD = \frac{|R - A|}{L} x100 \qquad \text{Equation 1}$$

Where:

CD = Either the upscale or zero calibration drift check.

R = Either the upscale or zero standard reference value

A = Either the Pb CEMS response to the upscale or zero standard

L = The emission limit expressed in the μg/m³

8.1.4. Flow Drift

If your Pb CEMS is an extractive type that uses a flow or volume measurement to determine the Pb concentration, a flow drift check must be performed at least once each day. During this flow drift check, the flow as measured by CEMS's primary flow or volume measurement device is compared to a secondary quality assurance flow measurement device that is used exclusively for the purpose of performing the flow drift check. The flow calibration drift is calculated according to Equation 2. The flow rate during the flow check must be the same as during normal sampling. The sample flow check may be performed over a time period shorter than the normal Pb CEMS sampling interval.

$$FD = \frac{|F_P - F_{QA}|}{F_{QA}} x100 \qquad \text{Equation 2}$$

Where:

FD = The flow drift as a percentage of the flow measured by the quality assurance flow meter.

F_p = The flow as measured by the primary flow measurement device in the Pb CEMS

F_{QA} = The flow as measured by the CEMS's secondary quality assurance flow meter.

8.2. Quarterly Audits

8.2.1. Frequency Requirements

Analyzer and flow (if applicable) audits must be performed at least once per calendar quarter. The minimum time between regularly scheduled quarterly audits shall be two months, while the maximum allowed time between quarterly audits shall be four months. Audits may occur more frequently if the audit is required to demonstrate the accuracy of the Pb CEMS following repair or adjustment.

8.2.2. Analyzer Audit

The analyzer portion of each Pb CEMS must be challenged with a NIST traceable or traceable-to-NIST standard for Pb. The analyzer calibration error (AE) is calculated by dividing the difference between the known concentration of the Pb audit standard (C_s) and the concentration reported by the Pb CEMS (C_c) by the known concentration of the Pb audit standard (Equation 3).

$$AE = \frac{|C_S - C_c|}{C_s} x100 \qquad \text{Equation 3}$$

8.2.3. Flow Audit

If your Pb CEMS is an extractive type that measures flow or volume and utilizes that flow or volume measurement as part of calculating the output value you must perform a flow calibration audit to determine the flow calibration error. During this procedure you must compare the Pb CEMS measured flow rate to the flow rate as measured by a NIST traceable reference flow meter. The flow rate during the audit must be the same as that used during normal instrument sampling. You must make at least three measurements of flow on both the Pb CEMS and the reference flow meter. For each measurement set calculate the flow calibration error (*FE*) dividing the difference between the flow as measured by the reference flow meter (F_s) and the flow as measured by the Pb CEMS (F_c) and divide it by the flow as measured by the reference flow meter (Equation 4). Then calculate the average error for each of the three measurements.

$$FE = \frac{|F_S - F_c|}{F_s} x100 \qquad \text{Equation 4}$$

8.3. Annual Linear Accuracy Audit

8.3.1. Frequency Requirements

Annual Linear Accuracy Audits for Pb CEMS are required annually. The minimum time between annual audits is nine months while the maximum time is 15 months.

8.3.2. Procedures

The linear accuracy audit is a dynamic spiking procedure in which the lead CEMS is challenged with a reference aerosol containing lead at several different concentration levels. The aerosol concentrations are produced using a Reference Aerosol Generator (RAG) and are introduced into the Pb CEMS transport line while it is sampling stack effluent. The concentrations reported by the CEMS are plotted against concentrations generated using a reference aerosol generator and a best fit linear regression curve is generated. The slope of this line is an indication of the accuracy of the Pb CEMS over a range of concentrations, while the correlation coefficient is an indicator of instrument precision

8.3.3. Spiking Location

The Pb reference aerosol must be introduced into the Pb CEMS transport line at a point as close to the probe tip as possible. In this way the entire Pb CEMS including, the transport line, flow system, analyzer and data recorder are challenged.

8.3.4. Reference Aerosol Generator

The reference aerosol generator used for the linear accuracy audit must comply with the specifications and procedures laid out in the Traceability Protocol for Certification of Reference Aerosol Generators.[2] This means that the expanded uncertainty in the concentration of the reference lead aerosol must not exceed 10%.

8.3.5. Transport Line Flow Measurement

The linear accuracy audit is a dynamic spiking procedure, meaning that the lead containing aerosol is introduced into the stack effluent sampled by the Pb CEMS. For this reason the total flow (sampled stack gas and reference aerosol) in the Pb CEMS transport line must be measured to determine the concentration of lead being sampled by the CEMS. Flow in the transport line may be measured in several ways. This procedure outlines two approaches: laminar flow elements and flow by dilution.

8.3.6. Laminar Flow

Prior to spiking, a calibrated laminar flow element may be inserted into the Pb CEMS's transport line downstream of all instrument sampling. The measured flow from the laminar flow element may be used to calculate the lead concentration being sampled by the Pb CEMS.

8.3.7. Flow by Dilution

Flow by dilution is a method of measuring flow where a concentration of a gas is quantitatively introduced into the flue gas stream and measured down stream by a calibrated instrument. For instance, a known concentration of propane can be quantitatively introduced into the flue gas stream and the diluted propane measured downstream using a gas chromatograph (GC). The calibration gas must be introduced into the gas stream quantitatively. Typically this is done by using a mass flow controller.

Prior to spiking the gas chromatograph or other measurement instrumentation must be calibrated at least three points through the expected measurement range. After the dynamic spiking procedure is completed the measurement instrument should be checked for bias at each of the four measurement points. The bias should be less than 5% of the expected value for each point.

The transport line flow (F_T) is related to the concentration of the spiked gas (G_s), flow rate of the spiked gas (F_s) and the measured gas concentration (G_M) using the following relationship (Equation 5).

$$F_T = \frac{G_s}{G_M} F_S \qquad \text{Equation 5}$$

8.3.8. Calculation of the Reference Lead Concentration

The reference aerosol generator (RAG) creates an aerosol of a known concentration which is then introduced into the Pb CEMS transport line which has a measured flow rate (Section 8.4.3.2). The concentration of lead produced by the RAG is therefore, diluted by the stack gas flow. This diluted concentration is the reference concentration then that should be measured by the Pb CEMS. This reference concentration (C_R) is calculated by multiplying the RAG produced aerosol concentration (C_{RAG}) by the ratio of the reference aerosol generator flow (F_{RAG}) to the total flow as measured (F_T) according to the procedures in Section 8.4.3.2 (Equation 6).

$$C_R \square \frac{F_{RAG}}{F_T} C_{RAG} \qquad \text{Equation 6}$$

8.3.9. Source Operation During Spiking

The linear accuracy audit procedures require that the background concentrations of lead be less than 15% of the applicable emission limit during the testing period. Therefore the source should be operated in a manner to prevent any lead emissions in excess of 15% of the emission limit (e.g. only burn natural gas). If this is not possible or if background concentrations of lead still exceed 15% of the emission limit even after taking reasonable steps to eliminate lead from the effluent emissions, it may be necessary to filter lead from the transport line upstream of the spiking location (e.g. use a particulate filter upstream of the spiking location).

8.3.10. Determination of Background Lead Concentrations

Prior to spiking determine the background concentration of lead as measured by Pb CEMS by taking nine measurements while the unit is operating in the manner described in Section 8.4.4. If necessary this background concentration of lead may be subtracted from the total lead as measured by the CEMS during spiking.

8.3.11. Pb CEMS Operation

The Pb CEMS must be operated normally throughout the course of the spiking procedures. This includes operating at normal flow rates and maintaining sampling times that are the same as those used during normal instrument operation.

8.3.12. Spiking Procedures

The instrument must be challenged at three different lead concentration levels as listed below:

1. Low – 10 to 30 percent of the emission limit
2. Mid - 40 to 60 percent of the emission limit
3. High – 80 to 120 percent of the emission limit

You may spike at more concentration levels and include them in the regression analysis if for example you want to demonstrate a higher instrument span.

At least nine valid measurements must be acquired at each concentration level. The first two measurements at each concentration level may be eliminated to allow for time for the reference aerosol concentration to stabilize.

8.3.13. Linear Least Squares Regression Analysis

Plot each Pb CEMS reported concentration against the reference lead concentration (C_R from Equation 6) and determine the slope, intercept and correlation coefficient of the best fit line. This best fit line will have the form as shown in Equation 7. The slope, intercept and correlation coefficient may be calculated according to Equations 8, 9 and 10 respectively.

$$\hat{y} = b_o + b_1 x \qquad \text{Equation 7}$$

Where:

$\hat{y}$ = Concentration output of the Pb CEMS as predicted by the linear least squares fit

b_1 = The slope of the best fit line

b_o = The intercept of the best fit line

x = The reference aerosol

$$b_1 = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^{n}(x_i - \bar{x})^2} \qquad \text{Equation 8}$$

Where:

b_1 = The slope of the best fit line

x_i = An individual reference aerosol Pb concentration

$\bar{x}$ = The average reference aerosol Pb concentration

y_i = An individual reported Pb CEMS concentration

$\bar{y}$ = The average reported Pb CEMS concentration

$$b_o = \bar{y} - b_1\bar{x} \qquad \text{Equation 9}$$

Where:

b_1 = The slope of the best fit line

b_o = The intercept of the best fit line

$\bar{y}$ = The average reported Pb CEMS concentration

$\bar{x}$ = The average reference aerosol Pb concentration

$$r = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \sum_{i=1}^{n}(y_i - \bar{y})^2}} \qquad \text{Equation 10}$$

Where:

r = The correlation coefficient

x_i = An individual reference aerosol Pb concentration

$\bar{x}$ = The average reference aerosol Pb concentration

y_i = An individual reported Pb CEMS concentration

$\bar{y}$ = The average reported Pb CEMS concentration

9.0 Performance Criteria and Out of Control Procedures

9.1. Calibration Drift Checks

9.1.1. Zero Drift Check Criteria

The zero drift must be less than 20% of the emission limit every day. If the Pb CEMS fails the zero drift check, immediately re-perform the zero drift check. If the Pb CEMS passes during the second check the CEMS may continue to operate. If it fails the second test the CEMS is out of control and the CEMS may require maintenance. Following the

CEMS repair, it must pass three zero drift checks before the CEMS is in control and can be used to monitor for Pb.

9.1.2. Upscale Drift Check Criteria

The upscale drift must be less than 15% of the emission limit every day. If the Pb CEMS fails the upscale drift check, immediately re-perform the upscale drift check. If the Pb CEMS fails the second check the CEMS is out of control and may require maintenance. Following repairs the CEMS must pass at least three consecutive upscale checks before it is back in control.

9.1.3. Flow Drift Check Criteria

The flow drift must be less than 15% of the flow as measured by the Pb CEMS quality assurance flow meter every day. If the Pb CEMS fails the first drift check, immediately re-perform the flow audit. If the CEMS fails the second audit the CEMS is out of control and may require maintenance. Following repair the CEMS must pass three consecutive flow audits before it is back in control.

9.2. Quarterly Audit

9.2.1. Analyzer Audit Procedures

When the analyzer calibration audit standard is analyzed the concentration of lead as reported by the Pb CEMS must be within 10% of the certified value of the analyzer audit standard. If the Pb CEMS fails the flow audit it is out of control and may require maintenance. Following maintenance the Pb CEMS must pass an analyzer audit before it is back in control.

9.2.2. Flow Audit Procedures

When the unit is operating at normal flow rates, the average flow as measured by the Pb CEMS flow meter must be within 10% of the flow as measured by a NIST traceable reference flow meter. If the Pb CEMS fails the flow audit it is out of control and may require maintenance. Following maintenance the Pb CEMS must pass a flow audit before it is back in control.

9.3. Linear Accuracy Audit

9.3.1. Test Criteria

Plot the Pb CEMS reported concentration versus the reference aerosol concentration. If the slope of the best fit line is between 0.85 and 1.15, the intercept is less than 20% of the emission limit, and the correlation coefficient is greater than 0.90 the Pb CEMS may be used without applying a correction factor. If the slope or intercept criteria fall outside of this range a correction factor may be applied to the Pb CEMS data provided the following three criteria are met.

1. The slope of the best fit line is not greater than 1.30 or less than 0.70.
2. The intercept is not greater than 40% of the emission limit
3. The correlation coefficient is greater than 0.90.

If both the slope and intercept need to be adjusted the concentration reported by the Pb CEMS may be adjusted using Equation 11.

$$C_c = \frac{C_U - b_0}{b_1} \qquad \text{Equation 11}$$

The slope may be adjusted using Equation 12.

$$C_C = \frac{C_U}{b_1} \qquad \text{Equation 12}$$

The intercept may be adjusted using Equation 13.

$$C_C = C_U - b_o \qquad \text{Equation 13}$$

For all three equations

C_C = The corrected Pb CEMS concentration (μg/m³)

C_U = The uncorrected Pb CEMS concentration (μg/m³)

b_0 = The intercept of the best fit line

b_1 = The slope of the best fit line

If the Pb CEMS fails the linear accuracy audit the CEMS must be repaired and must pass another linear accuracy audit before it can be used for compliance monitoring.

10.0 Reporting Requirements

At the reporting interval specified in the applicable regulation report the results of all drift checks and audits performed during the reporting interval. For each out of control period report the results of the drift check or audit that caused the out of control period and those results that demonstrate that the Pb CEMS is back in control. Document all repairs and corrective actions undertaken during the out of control periods.

11.0 References

1. Performance Specification ZZ. Specifications and Test Procedures for Lead Continuous Emissions Monitors on Stationary Sources. June 2011.

2. Siemers, A.; Petterson, K.A.; Cooper, J.A.; Barth, D.; *Draft Traceability Protocol for Certification of Reference Aerosol Generators.*; EPA Contract EP-D-05-096. April, 2011.

12.0 Tables and Graphs

Frequency	Test	Test Requirements	Test Criteria
Daily	Zero Drift	Daily Monitor the Zero Standard	< 20% drift each day
	Upscale Drift	Daily Monitor the Upscale Standard	< 15% drift each day
	Flow Drift	Monitor flow drift daily	< 15% drift each day
Quarterly	Analyzer Calibration Audit	Audit with Pb standard designed to challenge the analyzer portion of the Pb CEMS	< 10% difference between the CEMS reported value and the certified concentration
	Flow Calibration Audit	Check the flow or volume measurement of the Pb CEMS using a reference flow measurement device	<10% Difference between the flow measurement device and the CEMS measured flow
Annually	Linearity Audit	☐ Use a Reference Aerosol Containing a known concentration of Pb ☐ Dynamically Spike the stack gas sampled by the Pb CEMS ☐ Need at least 3 concentration levels which include a 2 fold concentration change and the emission limit ☐ Also include a zero or background concentration with no spiking. ☐ Spike into source, or spike into transport line as close as possible to the probe	☐ Slope = 0.85 to 1.15 ☐ $r \geq 0.90$ ☐ intercept < 20% of emission limit ☐ if the above criteria are met then no correction ☐ if not met apply a correction (correlation criteria must be met)

Appendix C

Traceability Protocol for Certification of Reference Aerosol Generators

DRAFT

EPA Contract EP-D-05-096, Assignment 4-07
EPA Project Manager: Daniel G. Bivins

MACTEC Work Order No. 201001192
MACTEC Project No. 688009S509

Submitted To:
MACTEC Federal Programs
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April 12, 2011

Executive Summary

A reference aerosol generator (RAG) produces an aerosol by nebulizing a solution of known concentration, at a measured rate, into a measured carrier gas flow to emit a NIST traceable aerosol of specific concentration. Uncertainties are defined for each input and a total, combined uncertainty value for the generated aerosol concentration is established. The reference aerosol can be used to challenge the accuracy of monitors designed to measure species contained in aerosols. These monitors include metals and particulate matter continuous emissions monitors (CEMS), ambient PM_{10} and $PM_{2.5}$ beta gauges, and metals continuous fence line monitors (CFLM). Typically gas monitors are challenged using NIST traceable gases, whose concentrations have been established using an unbroken chain of comparisons of a candidate gas standard to a primary NIST gas standard. However, no such primary NIST standards exist for analytes in aerosols. This document outlines the general requirements to certify and evaluate whether an aerosol concentration produced by a reference aerosol generator is traceable to NIST, and provides guidance on establishing uncertainty values for each input as well as the total expanded, combined, uncertainty value. In order to establish NIST traceability for a reference aerosol generator's output, this protocol requires that all measurements required to produce the aerosol are NIST traceable, including using solutions with NIST traceable concentrations, using NIST traceable gas flow meters, and using NIST traceable balances to measure solution loss rate. A total capture test should be conducted to certify the output concentration of the RAG by verifying the NIST traceable reference value to within 15% of the analytical method result. Periodic quality assurance (QA) and recertification protocol should follow as required by the manufacturer or the applicable regulation.

1. Introduction

A reference aerosol generator (RAG) is a device which produces an aerosol of known concentration of an analyte or analytes of interest. Calibration gases have traditionally been used to establish the accuracy of continuous gas monitors. However, no such primary NIST standards exist for analytes in aerosols. Instead, a reference aerosol generator can be used to establish the accuracy of monitors measuring aerosol analytes. A NIST traceable certified reference aerosol generator is a useful calibration and auditing tool for several types of monitors including particulate matter (PM) continuous emissions monitors (CEMS), multi-metals CEMS, metals continuous fence line monitors (CFLM), and ambient PM_{10} and $PM_{2.5}$ monitors.

Traceability of gas standards are typically established using an unbroken chain of comparisons of a candidate gas standard to a primary National Institute of Standards and Technology (NIST) gas standard. Instead of utilizing direct comparisons to NIST standards, this protocol relies on an approach of establishing NIST traceability for the individual components and measurements of a reference aerosol generator that are critical to establishing the analyte concentration. **This approach is similar to the approach EPA has taken recently to establish NIST traceability for mercuric chloride ($HgCl_2$) gas generators.**[1] This protocol borrows heavily from that document.

This Traceability Protocol for Certification of Reference Aerosol Generators proposes methods for: (1) establishing the initial NIST traceability and performance requirements of the key components of RAGs; (2) determining the uncertainty of each key component; (3) calculating NIST traceable output concentrations and the expanded, combined uncertainty values for the aerosol standards produced by the RAG; and (4) verifying the NIST traceable aerosol concentration with a total capture test and certifying the output of the RAG. The protocol also makes ongoing quality assurance (QA) recommendations.

Like the Interim EPA Traceability Protocol for Qualification and Certification of Oxidized Mercury Gas Generators (Protocol for $HgCl_2$ Generators), this traceability protocol sets a “target” expanded, combined uncertainty value of 10% for the generated aerosol standards. The NIST traceable RAG output concentration is verified using a total capture test. This protocol specifies that if the NIST traceable concentration is within 15% of the total capture test results, then the output of the RAG is considered certified as a NIST traceable reference aerosol generator. Like the $HgCl_2$ Protocol, this document does not explicitly require assessment of the sample transfer lines or any other measurement system component as they are not considered part of the reference aerosol generator. The total capture test is a practical tool for verification and certification of RAG output but does not in itself demonstrate traceability.

This protocol could potentially be used to establish NIST traceability and to certify RAGs used in a variety of air quality monitoring capacities as quality assurance and auditing tools for both ambient and source CEMS, but certain aspects of the document are written with respect to Cooper Environmental Services' (CES) Quantitative Aerosol Generator (QAG).

2. Qualification Tests

Manufacturers of RAGs are required to conduct qualification tests to demonstrate the performance of each RAG model prior to demonstrating NIST traceability and undergoing output certification. Documentation of the qualification test procedures and accompanying data should be available upon request to regulatory officials. The manufacturer is responsible for information and data that demonstrates that a RAG can operate reliably, with high precision and accuracy, over a range of conditions that could reasonably be encountered in the field application of the device.

2.1 Definitions

2.1.1 Aerosol

A suspension of solids and/or liquids in a gas

2.1.2 Reference Aerosol Generator (RAG)

A device which generates an aerosol with an analyte concentration that is traceable to NIST standards. This aerosol can then be used to audit or calibrate monitors and/or analytical methods measuring that analyte.

A reference aerosol generator produces an aerosol by nebulizing a solution containing a known analyte concentration, at a measured rate, into a measured flow. All of the inputs can be directly linked to NIST-traceable standards. A reference aerosol generator consists of the following components and modules:

1) Solution Delivery Module – This module includes any equipment necessary to contain and deliver the solution to the aerosol generation point. This module will often include a solution reservoir, solution delivery lines, a pump to generate flow, and a NIST certified balance.
2) Aerosol Generation System – This system includes all of the equipment required to aerosolize the solution. This could include nebulizers, compressed air, and electronic equipment.

3) An Evaporation Zone – This is the zone where the nebulized solution droplets are evaporated to remove liquid water.
4) Aerosol Dryer – This system consists of any of the components required to generate, measure, and treat the aerosol carrier gas flow. Key components could often include a pump or a blower, compressed air, flow meters, and valves.
5) An Electronic and Data Processing System – This system encompasses the specific electronic configuration of the RAG as well as hardware and software for instrument control and data processing

2.1.3 Expanded Uncertainty

As used in this protocol, expanded uncertainty is defined by two (2) times the total uncertainty or standard deviation σ_t

2.1.4 Nebulization, Aerosolization

To convert a liquid to a fine spray

2.1.5 Operational and Environmental Conditions

The manufacturer should provide information on the operational range or limitations of the RAG, specifying the conditions in which the model can be expected to operate reliably and meet all performance specifications for parameters such as:

2.1.5.1 Carrier Gas Supply

The minimum and maximum compressed air or nitrogen supply pressure, the acceptable variation in supply pressure, the necessary gas flow rate, and the quality of the carrier gas required

2.1.5.2 Back Pressure

The range of back pressures over which the generator has been tested and can deliver reliable aerosol concentrations

2.1.5.3 Enclosure Temperature Operating Range

The range of ambient temperatures over which the thermal stability of the generator has been tested and can deliver reliable aerosol concentrations. Alternately, the temperature range that must be maintained by on-board temperature controls for a RAG to deliver accurate and precise aerosol concentrations

2.1.5.4 Line Voltage

A range of acceptable line voltage limits in which the RAG can function reliably

2.1.5 Operation, Maintenance and QA

The manufacturer must provide standard operating procedures for the installation, start-up, operation, maintenance, and quality assurance of the RAG. The manufacturer must also identify the conditions and factors that would automatically require recertification of the RAG, such as known malfunctions, failures, component replacement, recalibrations, etc.

2.1.6 Laboratory Output Verification and Performance Tests

The manufacturer of the RAG should develop a report describing qualification tests performed to demonstrate that the RAG model will generate precise and accurate aerosol concentrations over a range of conditions. Specific tests include repeatability tests, thermal stability tests, supply pressure tests, line voltage variation tests, and generator output verification tests.

2.1.6 Range(s)

The minimum and maximum concentration range(s) of working solution in $\mu g/m^3$ and flow rate in liters per minute (lpm) over which the RAG has been demonstrated to meet performance specifications. Additionally, the description of the range should define the specific operating variables that must be selected and altered to establish the effective operating range and aerosol concentration.

2.1.7 Traceability to NIST

A documented procedure by which traceability of measurement results to a respective National Institute of Standards and Technology reference standard is established through an unbroken chain of comparisons, each having stated uncertainties. Comparisons are based on appropriate physical and chemical measurements

2.1.8 Total Propagated Uncertainty Equations[7]

a) $A + B = C \qquad \sigma_C = \sqrt{\sigma_A^2 + \sigma_B^2}$

b) $AB = C \text{ or } \dfrac{A}{B} = C \qquad \sigma_C = C\sqrt{\left(\dfrac{\sigma_A}{A}\right)^2 + \left(\dfrac{\sigma_B}{B}\right)^2}$

3. Reference Aerosol Generator Traceability, Initial Certification and Uncertainty Equations

3.1. Introduction

This section provides a protocol to establish NIST traceability for a reference aerosol generator by demonstrating NIST traceability of a RAG's key inputs. It also provides the methods and equations necessary to quantify the expanded, combined uncertainty of the RAG's output, as well as instructions for verifying the NIST traceable output of a RAG with a total capture test. A RAG that has performed and documented the following procedures and has met or surpassed the acceptance criteria satisfies the NIST traceability and certification requirements.

The key system components of a RAG include:

(a) A container for the working solution on the balance (reservoir)

(b) A balance that communicates directly with the on-board computer and establishes a measured solution loss rate

(c) A flow meter(s) and controller(s) to establish the flow rates of the carrier gas

Initial certification of a RAG requires NIST traceability through a clear, unbroken chain of comparisons for each of the key inputs of the RAG, as well as the determination of the expanded, combined uncertainty of the generated "reference value" concentration. The key inputs include solution concentration, the solution loss rate, and the carrier gas flow rate. For the solution concentration, NIST traceability is demonstrated through use of commercial NIST solution standards and following protocol when diluting NIST standards. For the solution loss rate and carrier gas flow rate, NIST traceability is demonstrated through calibration of the balance and flow meters with NIST standards.

A "reference value" of the concentration of each analyte in the aerosol can be calculated using Equation 1.

$$C_{Ai} = \frac{C_{Si} \times R_{Si}}{F}$$

Equation 1

Where:

C_{Ai} = The concentration of the i^{th} analyte in the reference aerosol (grams of analyte / m^3)

C_{Si} = The concentration of the i^{th} analyte in the NIST traceable solution (grams i^{th} analyte
per gram of solution)

R_{Si} = The solution loss rate for the i^{th} analyte (grams per minute)

F = The carrier flow for the aerosol (m^3 per minute)

NIST traceability for a reference aerosol generator is established through the traceability of the solution concentration, the traceability of the balance used to measure the solution loss rate, and the traceability of the aerosol carrier gas flow rate

It is assumed that all of the nebulized analyte within the NIST standard solution is emitted by the RAG as a NIST traceable aerosol at the “reference value” concentration. This is subsequently verified with a total capture test before the RAG is certified.

3.1 Solution Concentration

The primary input in generating a NIST traceable aerosol is the NIST traceable solution, which is the basis for the other comparisons. For a RAG to be certified, NIST traceable solutions must be employed. NIST traceable solutions are available commercially for many different types of analytes. These solutions are traceable to NIST standard reference materials (SRM), their concentration uncertainty values are typically known to within ± 1% or better, and they are known to be stable for long periods of time (at least a year). Because they are independently produced, well-characterized and widely available, it is best to use these types of solutions whenever possible. However, solutions may not be available for all analytes of interest or at the desired concentrations. It is also possible that other components of these solutions (such as acids) could be incompatible with the monitors being challenged with the reference aerosol. For these reasons other potential methods for demonstrating NIST traceability of a solution are necessary. Two other approaches for demonstrating the NIST traceability of the solution include:

1) Dilution or serial dilution of a commercially available NIST traceable solution

2) Determination of a solution concentration utilizing an appropriate analytical method

Any dilution of a commercially available NIST traceable solution should be done in a manner so that each measurement in the dilution process is traceable to NIST. This includes assuring that any gravimetric or volumetric measurements are done using balances and/or glassware that are NIST traceable. Also, all dilutions should be done using deionized water, with high resistivity (16 mega ohms or higher). If solutions are diluted with acid, they should be high purity and free from contaminates. Generally, acids that are listed as being for use in trace metal analysis are of sufficient purity. Dilutions will also increase the uncertainty of the RAG output. See section 3.1.1. and Equation 3 to calculate the increase in combined uncertainty due to dilution.

The NIST traceability of a solution can also be established by determining the concentrations of the analyte of interest in a solution using an appropriate analytical method. Examples of such analytical methods include, but are not limited to ICP, ICP-MS, and AA. Often these analytical methods operate by comparing the instrument response to a known NIST traceable solution concentration with the instrument response to the unknown concentration. To demonstrate NIST traceability using this approach, it is important to document the NIST traceability of the respective analytical method/instruments and to include this uncertainty in the combined uncertainty value of the respective working solution ($\sigma_{C_{Wi}}$). For the most sensitive laboratory analytical methods, $\sigma_{C_{Wi}}$ will usually be less than about 5%.

3.1.1 Calculating the Uncertainty of the Solution Concentration

If an undiluted, NIST traceable SRM solution is used in the RAG, the uncertainty is equal to the uncertainty in the labeled concentration, which is usually about ± 1%.

If a commercially available solution has to be diluted to create a working solution for the RAG, then the concentration of that working solution may be calculated with Equation 2.

$$C_{Wi} = \frac{C_{Si} \times M_S}{M_S^i}$$

Equation 2

Where:

C_{Wi} = The concentration of the ith analyte in the working solution to be aerosolized

C_{Si} = The concentration of the ith analyte in the stock solution

M_S = The mass of the stock solution

M_S^{t} = The mass of the solution after dilution

However, dilution of the NIST traceable SRM solution increases the combined uncertainty. Combined uncertainty in the working solution is based on the gravimetric and volumetric standard uncertainties as well as the uncertainty in the SRM solution. The uncertainty of the diluted working solution can be calculated using Equation 3:

$$\sigma_{C_{Wt}} = C_{Wt}\sqrt{\left(\frac{\sigma_{C_{St}}}{C_{St}}\right)^2 + \left(\frac{\sigma_{M_S}}{M_S}\right)^2 + \left(\frac{\sigma_{M_{S'}}}{M_{S'}}\right)^2} \qquad \text{Equation 3}$$

Where:

$\sigma_{C_{Wt}}$ = The uncertainty in the concentration of the diluted working solution

$\sigma_{C_{St}}$ = The expanded uncertainty of stock solution

σ_{M_S} = The uncertainty of the aliquot weight or volume (%)

$\sigma_{M_{S'}}$ = The uncertainty of the final, diluted standard solution weight or volume (%)

a) The uncertainty in the commercial standard σ_{St} is provided by the supplier, and given by the percent accuracy of the solution concentration, usually about ± 1%.

b) The uncertainty of the aliquot weight σ_{M_S}, as recommended by USEPA, is calculated by multiplying the estimated readability (such as .001 to .00001) of the balance by three, dividing that number by the measured aliquot weight, and converting the results to a percentage.

c) The uncertainty of the final, diluted working solution weight $\sigma_{M_{S'}}$ can be estimated by dividing the readability of the balance by three, dividing that number by the measured final aliquot weight, and converting the results to a percentage.

3.2 Liquid Flow Measurement and Solution Loss Rate

The solution loss rate (aerosolization rate or mass emission rate) is another key factor in controlling RAG output concentration, establishing NIST traceability, and certifying a RAG. For the CES Quantitative Aerosol Generator (QAG), the solution loss rate of the analyte-containing solution is determined using a NIST certified laboratory balance.

CES' QAG utilizes a sensitive balance that communicates directly to an on-board computer system. Before operation, the balance can be calibrated using NIST-traceable weights so that the data output of the balance is NIST traceable. The uncertainty of the balance and the associated data is given by the manufacturer, or alternately per EPA recommendations, by multiplying the readability of the balance by three, dividing that number by the weight or change in weight during the QAG run, and converting the results to a percentage.

3.2.1 Calibrating a Laboratory Balance and Determining Uncertainty

(a) Zero a three-place (or more accurate) balance and check its calibration against NIST traceable weights in the range of measurement appropriate for each solution loss rate determination. If necessary, calibrate the balance per manufacturer's recommendations.

3.2.2 Solution Loss Rate Equations

Some types of nebulization processes for CES' QAG cause solution evaporation without aerosolization of the salts dissolved in the solutions. This effect is minimized by using carrier gas that is saturated at the same temperature as the nebulization chamber. However this control is not perfect and it is necessary to make a correction to the solution loss rate to account for solution evaporation with aerosolization, which is usually on the order of 1%, and the uncertainty in this correction is small relative to the total solution loss rate. The measurements required to account for evaporation should also be traceable to NIST and well-documented in the standard operating procedures for the device. Consult the instrument's operating manual for further reference.

The equation for the solution loss rate R_{Si} for each analyte i in the reference aerosol is calculated using Equation 4 – 6 as noted below.

$$R_{Si} = C_{Si}(R_m - R_v)$$

Equation 4

Where:

C_{Si} = Concentration of the ith element in the in the NIST traceable solution (may be C_{Wi} for a diluted working solution)

R_m = Measured rate of solution reservoir mass loss (solution loss rate), determined as the slope of a linear least squares fit of the reservoir mass data over the period of a test or tests (g/min).

R_v = Rate of vapor loss (converted from mg/min to g/min), calculated from the following equation:

$$R_v = F_u\, m_W$$

Equation 5

Where:

F_n = Flow rate of the nebulizer air (slpm)

m_W = Mass of water lost from the nebulizing air (mg/l), calculated from the following equation:

$$m_W = m_{T_s} - m_{T_n}$$

Equation 6

Where:

m_{T_s} = Mass of water in a liter of air at T_s (mg/l), taken from established NIST certified reference sources[9];

m_{T_n} = Mass of water in a liter of air at T_n (mg/l), taken from established NIST certified reference sources[9]; where

T_s = Temperature of the nebulizer air at the aerosol size-selection cone

T_n = Temperature of nebulizer air at saturation

3.2.3 Solution Loss Rate Uncertainty Calculation

The uncertainty in the solution loss rate $\sigma_{R_{St}}$ can be determined using standard propagation of error methodologies in respect to Equation 4. The uncertainty values for the parameters are either calculated or provided by the manufacturer of the respective measurement device.

The uncertainty of the solution loss rate $\sigma_{R_{St}}$ can be determined using the following Equations 7 - 10:

$$\sigma_{R_{St}} = R_{St}\sqrt{\left(\frac{\sigma_{C_{St}}}{C_{St}}\right)^2 + \left(\frac{\sigma_{(R_m - R_v)}}{(R_m - R_v)}\right)^2}$$

Equation 7

And: $\sigma_{(R_m - R_v)} = \sqrt{(\sigma_{R_m})^2 + (\sigma_{R_v})^2}$
Equation 8

And: $\sigma_{R_v} = \sqrt{(\sigma_{F_n})^2 + (\sigma_{m_w})^2}$
Equation 9

And: $\sigma_{m_w} = \sqrt{(\sigma_{m_{T_s}})^2 + (\sigma_{m_{T_n}})^2}$ Equation 10

3.3 Carrier Gas Flow Measurement

The carrier gas transports the generated aerosol to the receptor. All carrier gas flows used to calculate the aerosol concentrations should be measured using NIST traceable flow meters. These flow meters are readily available, usually with specified calibration periods such as annually. An uncertainty value (σ_F) is provided by the manufacturer. If manufacturer data is not available, gas flow meters can also be calibrated and the uncertainty of the gas flow rate determined by using the procedure listed in steps (a) through (e) of this section. Before and after using a reference aerosol generator to calibrate or audit a monitor, all generator flow meters should be checked using an independent NIST traceable flow meter to verify their accuracy.

3.3.1 Calibrating Carrier Gas Flow Meters and Determining Uncertainty

(a) Install a laboratory standard device for flow meter measurement such as a digital bubble meter or a piston displacement device at the outlet of the calibrator. The flow measurement device must have a NIST traceable calibration and an accuracy of 1% or better. Operate the flow rate measurement device, making sure to follow all the manufacturer's instructions and specifications.

(b) Operate the RAG according to the manufacturer's instructions and allow the generator to run for enough time to equilibrate.

(c) Test the gas flow output of the RAG against the NIST traceable flow meter device. For each gas flow rate level, record the data emerging from the carrier gas flow meter on the RAG and the NIST traceable standard. Record at least ten pairs of readings.

(d) To determine the uncertainty of the gas flow rate meter (σ_F) on the RAG, calculate the relative standard deviation (RSD) of the gas flow data pairs at each level. If the RSD is less than or equal to 2%, the gas flow rate determination is considered acceptable.

(e) In the subsequent use of the flow meter, at each gas flow rate setting, compare the average of the NIST traceable flow measurements to the gas flow reading indicated on the RAG. If the difference of these values exceeds the uncertainty value σ_F, a linear correction value can be calculated which can calibrate the indicated gas flow rate. The linear correction can be: 1) a factor based on the ratio of the actual gas flow rate to the indicated flow rate; or 2) a combination of a factor with and adjustment value for zero offset. Record the linear correction, and utilize it until the gas flow rate measurement device is re-calibrated at the same operating level.

4. Combined, Expanded Uncertainty Calculations and Acceptance Criteria

4.1 Uncertainty of Reference Aerosol Generator

The uncertainty of the reference aerosol generated standard can be calculated using standard propagation of error analysis and a coverage factor of 2.

Therefore for Equation 1: Aerosol Standard "Reference Value" Concentration

$$C_{Ai} - \frac{R_{Si} \times C_{Si}}{F}$$

Where:

C_{Ai} = The concentration of the ith analyte in the reference aerosol (or C_{Wi})

R_{Si} = The solution loss rate for the ith analyte

C_{Si} = The concentration of the ith analyte in the NIST traceable solution

F = The carrier gas flow for the aerosol

The equation for uncertainty in the concentration of the generated aerosol with a coverage factor of 2 is Equation 11:

$$\sigma_{C_{Ai}} = 2C_{Ai}\sqrt{\left(\frac{\sigma_{R_{Si}}}{R_{Si}}\right)^2 + \left(\frac{\sigma_{C_{Si}}}{C_{Si}}\right)^2 + \left(\frac{\sigma_F}{F}\right)^2} \quad \text{Equation 11}$$

Where:

$\sigma_{C_{Ai}}$ = The uncertainty in the concentration of the ith analyte in the aerosol

C_{Ai} = The concentration of the ith analyte in the aerosol

$\sigma_{R_{Si}}$ = The uncertainty of the solution loss rate

R_{Si} = The solution loss rate

$\sigma_{C_{Si}}$ = The uncertainty in the SRM solution concentration ($\sigma_{C_{Wi}}$ if diluted (Equation 3))

C_{Si} = The concentration of the ith analyte in solution (C_{Wi} if diluted (equation 2))

σ_F = The uncertainty in the carrier gas flow rate

F = The flow rate of the carrier gas

4.2 Acceptance Criteria

Like the Protocol for $HgCl_2$ Generators, the acceptance criteria for the Traceability Protocol for Certification of Reference Aerosol Generators is targeted at an expanded, combined uncertainty of 10%.

5. Total Capture Test Output Verification and Certification

After NIST traceability is established through the use of NIST traceable inputs, calibration of key components and calculation of the combined, expanded uncertainty, a total capture test can be utilized to certify the output of the RAG by verifying that the generated aerosol concentration is within 15% of the NIST traceable reference value. A 15% performance criteria for the total capture test is reasonable due to the defined uncertainty of the NIST traceable reference value concentration and the uncertainty of analytical methodology employed by the total capture test. During a total capture test, a filter, free of contaminates (e.g. stretch Teflon), is placed at the end of the aerosol transport line (at a point as close as possible to the point where the aerosol is introduced into the audited monitor) in such a way that all the particulate matter is captured on the filter. The mass of each analyte on the filter can then be determined using appropriate analytical techniques. If preferred or necessary, an impinger method may also be utilized.

Appropriate analysis procedures will depend upon the analyte of interest. Methods for analysis of inorganic constituents may be found in the Compendium of Methods for the Determination of Inorganic Compounds (I.O.) in Ambient Air. Examples include X-ray Fluorescence (I.O. 3.3), inductively coupled plasma (ICP) spectroscopy (I.O. 3.4), inductively coupled plasma/mass spectrometry (I.O. 3.5), and proton induced X-ray emission (PIXE) spectroscopy (I.O. 3.6). Alternatively, the analyte concentration in the reference aerosol can be determined using a reference method.

6. Ongoing Quality Assurance and Re-certification

Periodic Quality Assurance (QA) tests in the field should also be conducted, verifying the output of the RAG to within 15% of the NIST traceable reference value, or to the specification set by the applicable regulation. The accuracy of the aerosol generator must be checked at each of the concentration levels used during the CEMS audit and at a zero concentration. This protocol recommends that recertification and calibration of the RAG occur at least annually, as needed, or as specified by the relevant regulations.

7. References

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